Trends in the recovery of phosphorus in bioavailable forms from wastewater

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Abstract: Addressing food security issues arising from phosphorus (P) scarcity is described as one of the greatest global challenges of the 21st Century. Dependence on inorganic phosphate fertilisers derived from limited geological sources of P creates an urgent need to recover P from wastes and treated waters, in safe forms that are also effective agriculturally - the established process of P removal by chemical precipitation using Fe or Al salts, is effective for P removal but leads to residues with limited bioavailability and contamination concerns. One of the greatest opportunities for P recovery is at wastewater treatment plants (WWTPs) where the crystallisation of struvite and Ca-P from enhanced biological P removal (EBPR) sludge is well developed and already shown to be economically and operationally feasible in some WWTPs. However, recovery through this approach is limited to <25% efficiency unless chemical extraction is applied. Thermochemical treatment of sludge ash produces detoxified residues that are currently utilised by the fertiliser industry; wet chemical extraction can be economically feasible in recovering P and other by-products. The bioavailability of recovered P depends on soil pH as well as the P-rich material in question. Struvite is a superior recovered P product in terms of plant availability, while use of Ca-P and thermochemically treated sewage sludge ash is limited to acidic soils. These technologies, in addition to others less developed, will be commercially pushed forward by revised fertiliser legislation and foreseeable legislative limits for WWTPs to achieve discharges of <1 mg P/L.

Dear Editor,

Please find attached our revised manuscript entitled **"Trends in the recovery of phosphorus in bioavailable forms from wastewater"** by Patrick M Melia, Andrew B Cundy, Saran P Sohi, Peter S Hooda and Rosa Busquets. We are very grateful to both reviewers for their comments and have made changes to the manuscript accordingly.

In relation to the reviewers' comments we have made changes to the conclusions, having reduced the text and ensured that the key points of the manuscript are clearly reflected – the abstract and highlights sections have been revised to reflect the conclusions more accurately and clearly. Other changes made include the reduction of some text from the introduction and early sections which drew attention away from the main arguments of the manuscript. Additionally, as requested by the reviewers, we have included new information regarding the economics of phosphorus recovery and made changes to sections that address the bioavailability of recovered phosphorus products. We now believe that this revised manuscript reflects the latest trends in the recovery of phosphorus from wastewater.

Thank you very much for considering this manuscript for publication. If you require any further information, please do not hesitate to contact me.

Best regards,

Patrick Melia, Dr Rosa Busquets & co-authors.

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COMMENTS FROM EDITORS AND REVIEWERS

Reviewer #1: This MS mainly review P recovery technologies currently used in WWTP processes and other emerging technological options, and the use of recovered P as a mineral-P substitute. A major revision will be necessary prior to its possible publication in Chemosphere.
Title:
The words "and sewage sludge" should be removed, since this MS reviewed the P recovery process from municipal effluent to final P product. The sewage sludge was produced during the EBPR process of municipal effluent.

Thank you to reviewer #1 for pointing this out, we have decided to change the title to "Trends in the recovery of phosphorus in bioavailable forms from wastewater".

Highlights:
Most of them are not true highlights of this MS. This section should be re-organized to emphasize those important conclusions or those interesting jobs finished in this review.

Yes, we agree with this point, especially after making some changes to the conclusions of this manuscript, where both you and reviewer #2 had asked for revision. Please see the changes made to the highlights which we feel now reflects the important conclusions of this revised manuscript.

Abstract:
It should be rewritten in order to show the important conclusions in this review.

Thank you for this comment. We have now rewritten the abstract to more clearly reflect the key findings in this manuscript. Please see changes to the abstract: p.2, l.23-37

Introduction
P 5, L72-79: This paragraph should be moved to the section "6 Bioavailability of recovered P products".

We agree with this comment, it makes more sense for the information to appear where you have suggested. This change has been implemented. This paragraph now appears on: p.34, l.619-625.

P7, L131 - P8, L161: These two paragraphs discussed the P recovery from erosion, runoff sources, and animal wastes. They are removed from the context or considerably simplified, since they are not the major questions discussed in this MS.

The authors agree with this and have removed these two paragraphs from the text as this review does not cover this – other reviewers have suggested to reduce the length of some sections too.

P9, L168-176: The paragraph discussed the possible contaminants in municipal wastewaters. "Hence, wastewaters generally require selective recovery processes to.....as fertiliser". However, it seems that no relative discussions on selective recovery processes in this MS.

We have made this change to the text. Please see: p.8, l.135-136. "Hence, wastewaters generally require recovery processes with a certain degree of selectivity to remove P into a solid form that can be safely and effectively used as fertiliser."

Since struvite is one of the main recovered products discussed, and the process has high degree of selectivity because it is obtained through crystallisation, we have additionally discussed this advantage. See p.24-25, l.445-448: "The crystallisation of struvite and other P-rich precipitates results in a very low degree of impurities. This is advantageous because the selectivity of this process leads to a safe product that can be applied to soil directly, despite the possible presence of heavy metals and other contaminants in the EPBR effluents."

Furthermore, the current revision of EU fertiliser regulation will limit the composition of recovered P salts and ashes. We have newly indicated this on p.24, l.430-435: "...the legislation however is currently under revision to include recovered P residues such as struvite, ashes and pyrolysis materials (European Commission, 2016; Huygens et al., 2017). This revision also limits the composition of fertiliser products in terms of impurities and level and bioavailability of nutrients, therefore selective routes to obtain these products will be beneficial.".

2.2 Chemical precipitation
P16, L279: Since "the two most obvious disadvantages of chemical recipitation are the requirements and cost of chemical additions, and ..... are often unsuitable for reuse due to the low recoverability of P.....", it seems unnecessary to provide so many relative information in this section. This section should be simplified. Anyway, this MS want to review the P recovery from WWTP.

We agree with both reviewers that this part could be simplified. We have removed the 16 lines which cited examples to illustrate the disadvantages of chemical precipitation because they were moving the focus of the discussion away. We have only made brief mention to the main relevant disadvantages of chemical precipitation, which now appears on p.11-12, l.207-210: "The two most obvious disadvantages of chemical precipitation are the requirement and cost of chemical additions, and the generation of large volumes of sludge that are often unsuitable for reuse due to the low recoverability of P and possible incorporation of contaminants in the P-rich precipitate.".

2.3 Enhanced biological phosphorus removal (EBPR) Can the authors provide the information on the P content in PAO-dominated activated sludge and conventional one, since the PAO is reported to able to accumulate more P in their cells?

We have included this new information on p.14, l.243-245: "Sludge, highly enriched in PAOs, can accumulate as much as 20% cell dry weight as P, compared with 1–2% in non PAO-enriched sludge (Tchobanoglous et al., 2014)."

3 Sludge enhancement and P recovery from sludge P19, L369-376: These questions have been fully discussed in the section "2.2 Chemical precipitation". Therefore, it should be removed.

We agree and thank the reviewer for pointing out this repetition. This is now the only section that includes this information (having removed and simplified the information provided in section 2.2).

7 Conclusions
This section is really too long and should be simplified to show some important conclusion. No discussions and no references should be presented here.

We are very grateful to both reviewers for this comment and appreciate that the original conclusion section was too long and presented too much new discussion. The conclusions section has been somewhat rewritten, the revised section is now much clearer and shorter in length, providing only

the key conclusions discussed throughout the manuscript. Please see changes to the conclusion from p.37.

Reviewer #2: In this manuscript, the authors firstly summarized the current technologies for the recovery of phosphorus from sewage and sludge. Furthermore, the authors noted that the bioavailability of phosphorus must be taken into account when recovered phosphorus is utilized in the agriculure. Before the publication, some parts of the manuscript should be improved:

1. The manuscript contains a lot of content about of the present phosphorus recovery technologies (many review papers have done this work), while the detailed information about the recoverd phosphorus products on the real agricultural industy was not sufficient.

We really appreciate this comment and received a similar comment from other reviewers regarding the first part of this comment. Much of the detail from the introduction and section 2.2 which discusses chemical precipitation has now been removed or simplified.

Regarding the second part of your comment, our first submission included information of commercial P-recovered products, which cover a period of 2008-2017 (Table 2) but we appreciate that we were not clear enough about their application within the agricultural industry, so we have tried to address this in more detail. Currently, many of these products cannot be sold as fertilisers in the EU (unless specifically designated by nation states). New text which discusses this issue has been introduced, please see p.24, l.428-435: "Current EU fertiliser regulation recognises only primary mineral-derived P products as fertiliser whereas the rest of these recovered P products cannot yet be labelled as such (European Union, 2003) – the legislation however is currently under revision to include recovered P residues such as struvite, ashes and pyrolysis materials (European Commission, 2016; Huygens et al., 2017). This revision also limits the composition of fertiliser products in terms of impurities and level and bioavailability of nutrients, therefore selective routes to obtain these products will be beneficial.".

We additionally provide new information about specific examples of recovered P products which have commercial application for use within the fertiliser industry. See p.26, l.480-484: "Waternet, Amsterdam, which recovers P as struvite from bio-P sludge using the Airprex® process, reportedly makes an annual saving of €500 000 due to improved dewatering and reduced scaling problems – the recovered struvite product is sold to the fertiliser industry for between €50–100/t for fertiliser production (Waternet, 2017)".

We feel that the section discussing the bioavailability of recovered P residues (section 6, p.34-) gives a good overview of studies that assess the plant uptake of P from a variety of P-rich recovered products such as struvite, Ca-P, sewage sludge ash and thermochemically treated ash, compared with triple super phosphate and rock-P. However, we have newly included an additional section of discussion in section 6 (p.36, l.678-684): "It is additionally important that both the removal process and reuse of P are considered on a case-by-case basis – not all recovery processes will be applicable to all wastewaters, and similarly not all recovered products will be equally effective across different soil environments. As sorbent materials can be derived from a wide variety of materials and processes, providing a myriad of physical and chemical characteristics, P sorbed to and within the surface and structure of these solids may have wide ranging applications.".

2. The authors may introduce and emphasize more information about the bioavailability of phosphorus. For example, which recovered phosphorous products is the ideal option for the

agriculture. As we know, in some case, recovered phosphorus product could be applied as slow-release phosphorus fertilizer.

We agree with the reviewer that bioavailability of P and not P content in P recovered products is essential. A section discussing bioavailability (section 6, p.34-) includes a comparison between recovered P products (struvite, Ca-P, ashes, treated ashes) compared to triple super phosphate and rock-P, factors such as pH are also discussed. We have also newly introduced the following text in this section which introduces bioavailability of P in soils, see p.34, l.619-625: "Not all P in soil is bioavailable to plants and P is a key limiting nutrient in terrestrial ecosystems (Elser, 2012; Maltais-Landry et al., 2014). Phosphorus therefore plays a critical role in productive agriculture (Withers et al., 2014), but its plant availability however can often be low: it forms sparingly soluble fractions due to adsorption, precipitation or conversion to organic fractions in soil (Werner and Prietzel, 2015), via geochemical processes that depend on several soil properties such as the abundance of Ca, Al and Fe oxides, pH and organic matter content."

Additionally, we have introduced a new aspect to the discussion in this section which I mentioned in answer to your previous comment, see (p.36, l.678-684).

Within section 4 we have introduced two sentences that related to the applicability of struvite as fertiliser, see p.24, l.435-436 and p.24-25, l.445-448: "Among the recovered products in Table 2, struvite stands out due to its usability directly as a slow release fertiliser (Bouropoulos and Koutsoukos, 2000)" and "The crystallisation of struvite and other P-rich precipitates results in a very low degree of impurities. This is advantageous because the selectivity of this process leads to a safe product that can be applied to soil directly, despite the possible presence of heavy metals and other contaminants in the EPBR effluents", respectively.

3. The authors maybe compare the economics of different recovered technologies in detail.

We recognise that this is an essential point of the recovery of P from wastewater. We would love to provide a direct comparison on the economics of each approach however this is difficult to do due to the different levels of commercialisation of each technology. It becomes increasingly difficult to compare economics as many recovered products are yet to be marketed, the profitability/benefits to recovering P are currently associated with savings at the WWTP (such as reduced dewatering cost, scaling, etc.) which differ case-by-case. Where possible, we have included specific information about the recovery of struvite from a WWTP in Amsterdam which make savings of €500 000 per year, see p.26, l.480-484: "Waternet, Amsterdam, which recovers P as struvite from bio-P sludge using the Airprex® process, reportedly makes an annual saving of €500 000 due to improved dewatering and reduced scaling problems – the recovered struvite product is sold to the fertiliser industry for between €50–100/t for fertiliser production (Waternet, 2017)".

Additionally, the treatment of ashes is also economically favoured, and a specific example of this has been briefly introduced, see p.20-21, l.408-413: "The release of P from SSA can be achieved by the dissolution of the ashes in acid, the separation of heavy metals and the precipitation of calcium phosphate, ferric hydroxide and aluminium hydroxide, as in the Ash2®Phos process. This process is reportedly economically profitable since it is dealing with a waste which would otherwise incur a cost for disposal and the commercial products produced (mono/di-ammonium-phosphate and Fe and Al precipitants) (EasyMining-Sweden, 2017)".

4. In the part of conlusions, the text is a little long and the authors maybe make a clear viewponit.

Thank you for this comment. Both reviewers made similar comments regarding the conclusion. We appreciate that the original conclusion section was too long and presented too much new discussion. The conclusions section has been somewhat rewritten, the revised conclusion section is much shorter in length and provides only key and clear viewpoints as you have suggested. Please see changes to the conclusion from p.37.

In conclusion, I approve of its publication after major revision.

Trends in the recovery of phosphorus in bioavailable forms from wastewater

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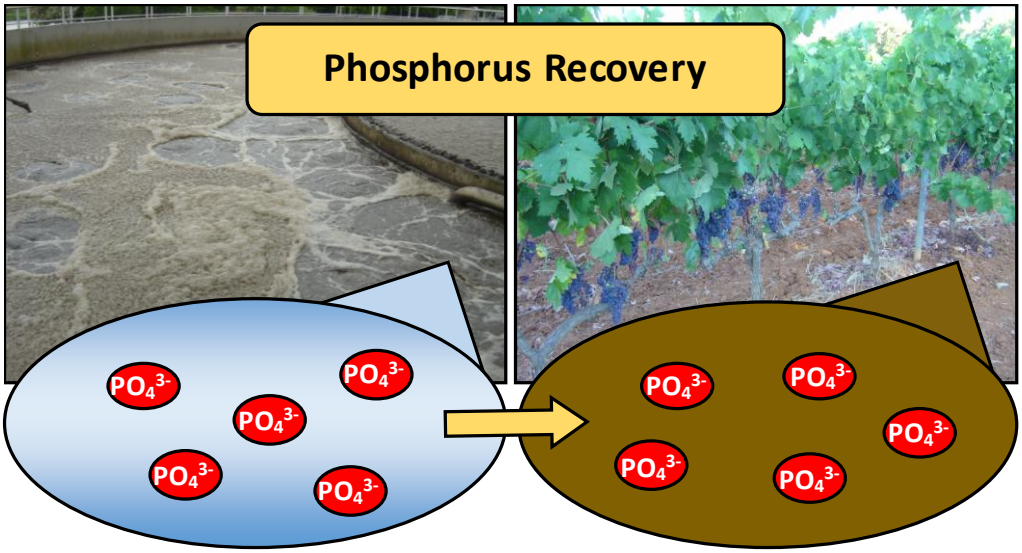
Abstract

Addressing food security issues arising from phosphorus (P) scarcity is described as one of the greatest global challenges of the 21st Century. Dependence on inorganic phosphate fertilisers derived from limited geological sources of P creates an urgent need to recover P from wastes and treated waters, in safe forms that are also effective agriculturally – the established process of P removal by chemical precipitation using Fe or Al salts, is effective for P removal but leads to residues with limited bioavailability and contamination concerns. One of the greatest opportunities for P recovery is at wastewater treatment plants (WWTPs) where the crystallisation of struvite and Ca-P from enhanced biological P removal (EBPR) sludge is well developed and already shown to be economically and operationally feasible in some WWTPs. However, recovery through this approach is limited to <25% efficiency unless chemical extraction is applied. Thermochemical treatment of sludge ash produces detoxified residues that are currently utilised by the fertiliser industry; wet chemical extraction can be economically feasible in recovering P and other by-products. The bioavailability of recovered P depends on soil pH as well as the P-rich material in question. Struvite is a superior recovered P product in terms of plant availability, while use of Ca-P and thermochemically treated sewage sludge ash is limited to acidic soils. These technologies, in addition to others less developed, will be commercially pushed forward by revised fertiliser legislation and foreseeable legislative limits for WWTPs to achieve discharges of <1 mg P/L.

Keywords:

Phosphorus recovery; wastewater; sewage sludge; struvite; sorption; bioavailability.


Phosphorus Recovery
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1 Introduction

Phosphorus (P) is an essential plant nutrient and makes up around 0.2% of plant dry weight (Jiang and Yuan, 2015; Schachtman et al., 1998). In aquatic ecosystems, low concentrations of P benefit the biological productivity of freshwater lakes, reservoirs and rivers. Concentrations of just ~0.02 mg P/L can be considered to cause eutrophication (Correll, 1998), having negative ecological effects where promoted algal growth (Yao et al., 2013) can cause hypoxia and negative effects from algal toxins (Bláha et al., 2009; Žegura et al., 2011).

Negative impacts within ecosystems caused by an excess of P has led governments to limit the P concentration in waters. As a whole, the Water Framework Directive 2000/60/EC (European Commission, 2008) in conjunction with the Council Directive 91/271/EEC concerning urban wastewater treatment (European Commission, 1991), identify sensitive areas where high levels of P would have large ecological impacts – and enforce the control of P in wastewater discharges, respectively. As an annual average, it is required that P concentrations within wastewater effluents are below 1–2 mg P/L, depending upon the sensitivity of the receiving environment and the size of the wastewater treatment plant (WWTP), or are reduced by 80% from the influent concentration (European Commission, 1998, 1991). Austria, Germany and Switzerland have now made P recovery mandatory from municipal sewage sludge (European Sustainable Phosphorus Platform, 2017).

The P loading within many ecosystems is a result of P discharges from WWTPs or the use of P in agriculture. Figure 1 summarises key P flows and losses throughout the global agricultural production and food consumption system. The inorganic P cycle is extremely inefficient and wasteful. Losses of P to natural water bodies from wastewater discharge represents approximately 10 % of inorganic P derived fertiliser applied to arable soil globally (see “A” in Figure 1). These losses create both a need and an opportunity, with respect to P

recovery and re-use, needed not only to ensure good ecological status of waterways, but also to maintain the global productivity of agriculture.

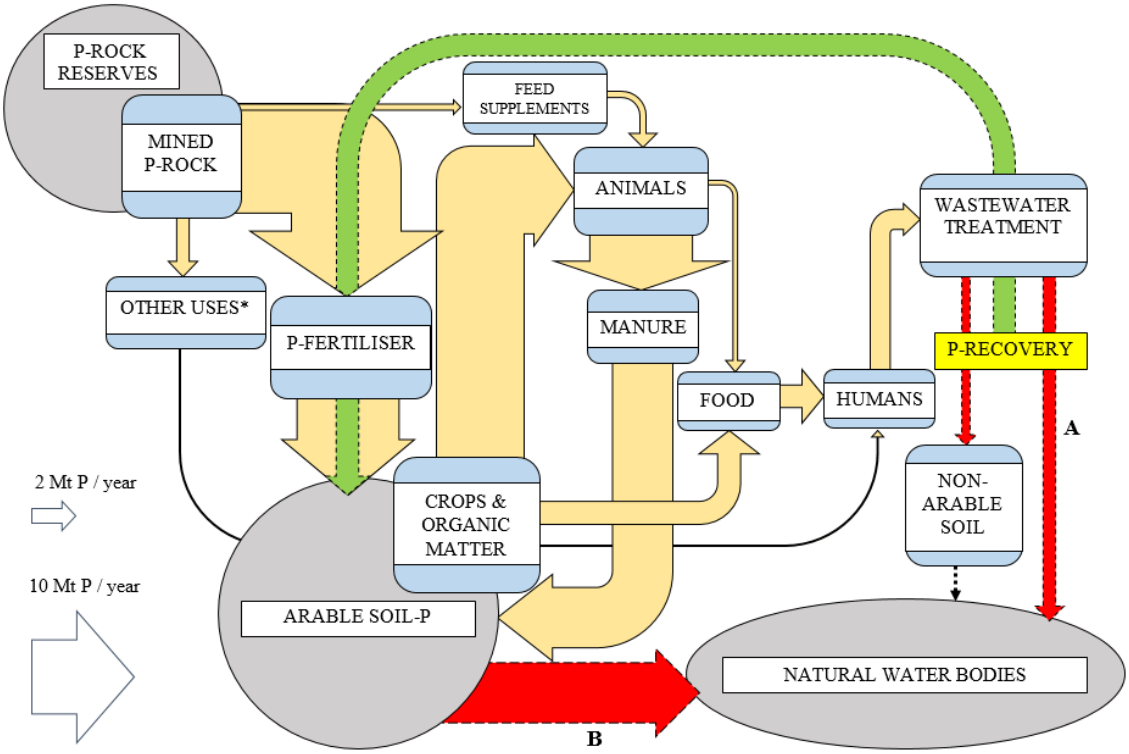

Figure 1. Diagram of key P flows. The widths of the arrows semiquantitatively represents figures reported by Cordell et al. (2009) in million tonnes (Mt) of P per year. Yellow, red and green arrows represent flows of P between major points of use in the food production and consumption system; key P losses and the potential flow of recovered-P from WWTPs, respectively. Losses such as those arising from fertiliser production and distribution, agricultural residues, and food chain losses are not shown. The blue boxes indicate major points of use. The grey ovals indicate major P sinks. Point "A" denotes the flow of P contained in treated or untreated sewage to natural water bodies and represents approximately 1.5 Mt P/year. Point "B" denotes the flow of P contained in erosion losses and is about 8 Mt P/year. *Other uses includes industrial uses such as the production of some detergents.

With increasing global populations and increased difficulty in accessing P reserves, many studies have raised concerns regarding depletion of mined P sources (Childers et al., 2011; Cordell et al., 2011, 2009; Cordell and Neset, 2014; Gilbert, 2009; Smil, 2000; Withers et al., 2014). Mined P rock exists mostly in ancient marine sedimentary deposits, the majority of

111 which are situated in Morocco and Western Sahara (Van Kauwenbergh et al., 2013).
112 Estimated at ca 67 000 Mt (USGS, 2014), the global production of P rock is widely thought
113 to hit a peak this century (Walan et al., 2014), with some predicting that economically
114 mineable P rock reserves could become scarce or exhausted within 100 years (Childers et al.,
115 2011; Cooper et al., 2011; Smil, 2000). The decreasing quality of P rock, in terms of
116 contamination with cadmium for example (Mar and Okazaki, 2012), and price spike events
117 (Mew, 2016) are additional concerns. With an expanding global population relying on
118 decreasing and deteriorating P resources, the development of technologies for improved
119 recovery and re-use of P is becoming an increasingly urgent environmental, economic and
120 societal issue. The rising cost of P rock extraction will inevitably favour the development of
121 these technologies.

122 WWTPs provide one of the biggest opportunities for P recovery (Schoumans et al., 2015;
123 Smil, 2000) given the relatively high and constant P load in sewage. The recovery of P from
124 wastewaters can provide an array of benefits: (1) meeting the effluent P limits required by
125 legislation; (2) reducing eutrophication problems; and (3) providing a potential source of
126 fertiliser of agricultural and economic value. The latter simultaneously reduces the reliance
127 on inorganic (rock-P derived) fertilisers in agriculture.

128 However, municipal wastewaters contain many contaminants, both organic and inorganic,
129 including heavy metals and metalloids (Nguyen et al., 2013), pesticides (Köck-Schulmeyer et
130 al., 2013), pharmaceuticals (Antoniou et al., 2013), personal care products (Brausch and
131 Rand, 2011), nanomaterials, perfluorinated compounds (PFCs) (Richardson and Ternes,
132 2014), hormones (Loos et al., 2013), recreational drugs (Wilkinson et al., 2016) and
133 pathogens (Cai and Zhang, 2013). Therefore, the application of untreated effluent to
134 agricultural land would pose associated risks to human food consumption (Schoumans et al.,

2015). Hence, wastewaters generally require recovery processes with a certain degree of selectivity to remove P into a solid form that can be safely and effectively used as fertiliser.

Here we critically review P recovery technologies currently used in WWTP processes (chemical precipitation, enhanced biological P removal (EBPR), various sludge treatments, struvite and Ca-P crystallisation, and thermochemical treatment) and other emerging technological options, particularly with respect to recovery efficiency and the use of recovered P as a mineral-P substitute. We conclude this review by providing some recommendations for future work, namely the diversification of technological approaches to recover P and further consideration of the bioavailability and potential contamination of recovered products.

2 Management of P within WWTPs

2.1 Capture and accumulation of P – an overview

P exists in a variety of forms within wastewater and these vary throughout the WWTP process; P in particulate forms are more easily and completely removed through clarification steps (Dueñas et al., 2003) whereas dissolved P species, both organic and inorganic, require more targeted chemical or biological processes for their removal. P concentrations reported for municipal wastewaters are generally below 10 mg P/L (Kim and Chung, 2014; Petzet and Cornel, 2013; Qiu and Ting, 2014; Yuan et al., 2012).

Preliminary screening is firstly applied in WWTPs to remove larger particles followed by a primary treatment step. This involves the settlement and removal of suspended solids and organic fractions, which can be achieved by chemical addition or filtration (Tchobanoglous et al., 2014). Petzet and Cornel (2013) report that 17–26% of an incoming total P load, predominantly in particulate forms, can be transferred to primary sludge in initial settlement

158 at a WWTP. Secondary treatment, especially in larger WWTPs and those discharging to
159 sensitive environments, is then applied (European Commission, 1991). This can involve the
160 use of microbes to break down soluble organic compounds that remain after the preliminary
161 and primary treatment steps (through trickling filter beds or other treatments), and/or the
162 addition of chemicals to promote the coagulation and flocculation of solids. Other than
163 particulate P removed here through secondary clarification, specific P removal techniques
164 such as chemical precipitation or enhanced biological phosphorus removal (EBPR) can be
165 integrated into the treatment process to target dissolved forms of P. Tertiary and advanced
166 treatments are applied for the further removal or degradation of dissolved contaminants,
167 especially when the treated water will be reused. Aside from addressing ecological and
168 statutory issues, P removal at WWTPs prevents the build-up and blockage of pipes by
169 crystalline deposits and precipitates of P (De-Bashan and Bashan, 2004; Rittmann et al.,
170 2011).

171 Standard primary and secondary treatments often do not remove sufficient P to meet the
172 required discharge concentration. Under normal secondary treatment (the activated sludge
173 process) around 31–48% of influent P can be transferred into sludge (Petzet and Cornel,
174 2013). With the P removed through primary settlement, this can leave up to approximately
175 50% of the total influent P load to be removed by an enhanced P removal technique before
176 discharge into a receiving water body (Desmidt et al., 2015).

177 Techniques specifically used to remove P from wastewaters can be operationally categorised
178 as chemical, biological or physical. They include the established techniques of chemical
179 precipitation and enhanced biological phosphorus removal (EBPR). In each case P is
180 removed by the conversion of the various dissolved P forms into a solid (De-Bashan and
181 Bashan, 2004).

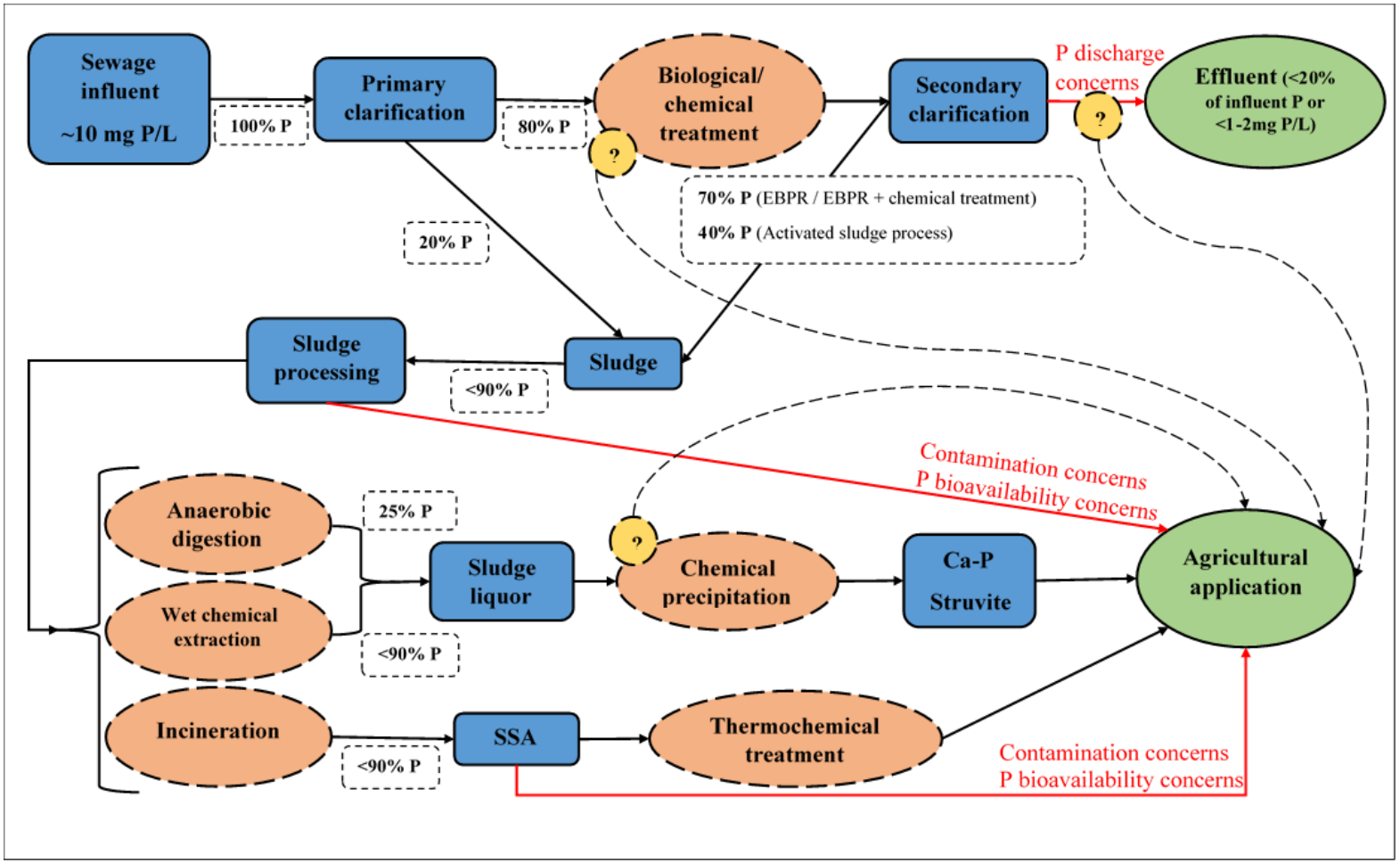

Figure 2. The flow of P through a typical WWTP process, the positions of P recovery technologies (dashed circles) and routes of application of recovered P to agriculture with concerns highlighted in red. Percentage of P (white boxes with dashed line) represents what can be approximately assumed to be removed or carried over to the next treatment stage as a percentage of the influent P load. The dashed yellow circles with question marks indicate where emerging technological approaches could target P recovery.

2.2 Chemical precipitation

Precipitation was first attempted to control eutrophication problems in the 1950s (Morse et al., 1998) and is the main commercial approach to P removal today (Wendling et al., 2013). The precipitative removal of P is usually achieved through the addition of di- or trivalent metal salts of Fe, Al or Ca (Table 1). P in the form HPO_4^{2-}, $H_2PO_4^-$ or H_3PO_4 (dependent upon reaction pH), as well as organic P and particulate P fractions, are coagulated to form a metal phosphate sludge and subsequently removed after flocculation and settlement. Chemical precipitation is more efficient at earlier stages in the waste water treatment process when the concentration of P in solution is highest. Processes involving seeded precipitation, where crystallisation is encouraged and controlled through the addition of a seed material, are being developed to offer more efficient and less costly treatment (Petzet et al., 2012; Song et al., 2006).

Fe and Al salts are considered the most suitable and are generally added as chlorides or sulphates (Morse et al., 1998), calcium can also be used and is generally added as lime ($Ca(OH)_2$). Fe salts are generally preferred as they are cheaper than Al – Fe-P chemistry relating the municipal wastewater is discussed in detail elsewhere (Wilfert et al., 2015).

In terms of emerging options, a recent study has investigated the use of potassium ferrate for P precipitation combined with water disinfection (Kwon et al., 2013). The latter arises from its status as a powerful oxidant while precipitation and coagulation of Fe-P occurs through reduction of Fe (VI). The disinfection rate obtained was faster than for chlorine of the same concentration. Within secondary effluent (1.46 mg total P/L), ferrate was able to remove more than 80% of P in the dosage range of 5–25 mg Fe/L. The two most obvious disadvantages of chemical precipitation are the requirement and cost of chemical additions,

and the generation of large volumes of sludge that are often unsuitable for reuse due to the low recoverability of P and possible incorporation of contaminants in the P-rich precipitate.

Table 1. Details of the three metals conventionally used in the chemical precipitation of P in WWTPs, including the optimal pH for the process, the most common precipitates formed and the advantages and disadvantages of using each.

Element	Optimal pH	Most common precipitate form	Advantages	Disadvantages
Fe	4.5–5 (Thistleton et al., 2002)	Strengite ($FePO_4 \cdot 2H_2O$) (Grzmil and Wronkowski, 2006)	• Relatively inexpensive • Effective in the precipitation of P	• Precipitate unsuitable for use as fertiliser.
Al	~6 (Lin and Carlson, 1975)	Variscite ($AlPO_4 \cdot 2H_2O$) (Lin and Carlson, 1975)	• Most effective precipitant. (Yeoman et al., 1988) • At pH 6, both biological treatment and precipitation with Al could be operated.	• Expensive • Precipitate unsuitable for use as fertiliser • Doses of >60mg Al/L have a toxic effect on autotrophic bacteria within a membrane bioreactor (Zahid and El-Shafai, 2012) – dosage must be carefully considered.
Ca	>10.5 (Jenkins et al., 1971)	Hydroxyapatite ($Ca_5(PO_4)_3OH$)	• Relatively inexpensive • Ca-P precipitates can be similar in form to rock-P and suitable for use in industry • Potentially suitable as fertiliser	• High pH requirement • High pH can create detrimental conditions for biological treatment • Additional neutralisation step may be required • Large volume of generated sludge

Numerous by-products and wastes have also been investigated as potential precipitants. Red mud, an abundant mining waste, has been studied for its potential for precipitation of P due to its high content of Al and Fe. Through the treatment of red mud, Poulin *et al.* derived a solid product that had P removal efficiency similar to commercial coagulants, namely 70–98% in solutions containing 5–100 mg P/L respectively (Poulin et al., 2008). Municipal solid waste fly ash has also been investigated, with reported removal rates of approximately 6 mg P/g (Zhong et al., 2014). Hydrated oil shale ashes in subsurface flow filters have been assessed in long period pilot-scale experiments treating municipal and landfill leachate wastewater in Estonia, achieving 99% removal from wastewaters ranging in P concentration from 0.13–17.0 mg total P/ L (Kõiv et al., 2010). In this case the direct precipitation of Ca-P was suggested to be the controlling P removal mechanism.

Other waste materials providing strong precipitation effects include calcined waste paper sludge. The formation of brushite ($CaHPO_4 \cdot 2H_2O$) was found to be the main mechanism controlling P removal in a laboratory scale study, which reached 1.5 mmol P/g (46.6 mg P/g) calcined paper sludge (Wajima and Rakovan, 2013). Drinking waterworks sludge was also found to be effective for P removal in laboratory scale experiments due to its high content of Al and Fe: 99% removal could be achieved from an initial concentration of 2 mg P/L and a sludge dose of 10 g/L in synthetic wastewater, at pH value 5–6 (Yang et al., 2014).

2.3 Enhanced biological phosphorus removal (EBPR)

EBPR was developed during the 1970s (Barnard, 1975; Yuan et al., 2012), and is extensively used today. Most full-scale P recovery technologies currently applied require the pre-accumulation of P (as bio-P sludge) using EBPR processes. EBPR relies on polyphosphate accumulating organisms (PAOs) or denitrifying PAOs to accumulate P intracellularly as polyphosphate granules, thus avoiding any requirement for chemical precipitants (Oehmen et

al., 2007; Wong et al., 2013). The process is enabled by alternating anaerobic and aerobic conditions; PAOs take up volatile fatty acids under the anaerobic phase, which are stored as polyhydroxyalkanoates and subsequently metabolised in the aerobic phase to supply the energy needed by the PAO to accumulate P (Kristiansen et al., 2012). Sludge, highly enriched in PAOs, can accumulate as much as 20% cell dry weight as P, compared with 1–2% in non PAO-enriched sludge (Tchobanoglous et al., 2014). Bacterial genus *Acinetobacter* was at first thought to be the primary PAO (Fuhs and Chen, 1975) in EBPR, however members of Actinobacterial genus *Tetrasphaera* (Kong et al., 2005) and the bacteria *Candidatus Accumulibacter Phosphatis* (He and McMahon, 2011; Hesselmann et al., 1999) are now considered to be more responsible for P accumulation in WWTPs (Kristiansen et al., 2012). In addition to bacterial strains, microalgae have been investigated as suitable PAOs for P assimilation in wastewater treatment (Solovchenko et al., 2016).

The accumulation of P within bio-P sludge and its settlement can facilitate the recovery of P and allow for direct utilisation as fertiliser, depending on contaminants present. Alternatively, further treatment can facilitate the solubilisation and recovery of P in a form such as struvite ($MgNH_4PO_4 \cdot 6H_2O$) (Baur, 2009). A recent paper investigated the use of microalgae and cyanobacterial strains for the accumulation of P from parboiled rice mill effluent. These P enriched PAOs showed moderate P release as a biofertiliser and was comparable to that of commercial fertilisers (Mukherjee et al., 2015).

In full scale WWTPs, EBPR processes can typically remove over 85% of P in municipal wastewater influent, often to concentrations <0.1mg P/L (Gautam et al., 2014; Gebremariam et al., 2011). Although efficient in many cases, there are however questions over the stability of its performance (Oehmen et al., 2007; Zheng et al., 2014). Various process inefficiencies and failures are reported to be associated with EBPR. One of the largest causes of deterioration and failure in EBPR systems arises from the occurrence of glycogen

accumulating organisms (GAOs) (López-Vázquez et al., 2008), which compete with PAOs for carbon substrate (Oehmen et al., 2007; Yuan et al., 2012). GAOs can function under aerobic or anaerobic conditions (Zheng et al., 2014) and are found widely in EBPR processes (Burow et al., 2007). Considerable effort has therefore been focused on establishing the conditions that might limit their growth (Oehmen et al., 2006, 2005, 2004; Wang et al., 2010; Whang and Park, 2006, 2002; Whang et al., 2007). This has established that at pH 8, the abundance of GAOs is restricted while optimal PAO activity is maintained (Oehmen et al., 2005). The type of carbon substrate and its concentration is also important (Shen and Zhou, 2016); propionate for example was found to be more beneficial than acetate for PAO growth (Wang et al., 2010; Zeng et al., 2013). The presence of toxic substances in the influent, such as Cr (VI) (≥0.5 mg/L), can also inhibit P removal, being toxic to PAOs (J. Fang et al., 2015).

Without carbon addition to ensure high and constant concentrations, the EBPR system can be very susceptible to changes in the influent composition. Consequently, climates with a tendency for sporadic heavy rainfall, which can drastically perturb nutrient concentrations, can affect biological P removal (Manyumba et al., 2009). The addition of organic carbon to the process however is unfavourable as it incurs additional cost to the EBPR process and increases the overall carbon footprint (Guerrero et al., 2015). Organic carbon additions derived from waste sources have been successfully investigated which may reduce cost and increase the sustainability of the process; waste activated sludge fermentation liquid was found to be a more effective carbon source that acetic acid (Ji and Chen, 2010), crude glycerol, a biodiesel waste product, was successfully dosed in an EBPR process and resulted in better control over P removal (Guerrero et al., 2015).

High temperatures, 30°C as opposed to 20°C, encourage GAO growth (Whang and Park, 2002) with lower temperatures found to be beneficial for PAO growth (López-Vázquez et al., 2008) and therefore P removal. Low aeration rates and thus low dissolved oxygen (DO) also

favour PAOs over GAOs (Carvalheira et al., 2014). These variables may impact on the final P concentrations in the treated effluents and discharges may exceed those permitted by legislation.

EBPR processes are considered to be a more sustainable compared to chemical processes and can often offer significant economic advantages in larger WWTPs (Manyumba et al., 2009). EBPR requires less or no chemical addition and has the potential for the full-scale recovery of P. However, where process inefficiencies are frequent and/or legislation requires consistently low P concentrations in effluent discharge, it is also common for larger WWTPs to deploy chemical precipitation in conjunction with EBPR to ensure requirements are consistently met (Kim and Chung, 2014; Kwon et al., 2013). This reduces the amount of P that can be solubilised and recovered through bio-P sludge digestion or direct application as fertiliser. Other limitations include the complexity of operations and a large energy and space requirement (Nguyen et al., 2014a). The future use of EBPR processes may therefore not extend beyond those WWTPs with a relatively narrow geographic, spatial and economic context.

3 Sludge enhancement and P recovery from sludge

A major disadvantage of chemical precipitation of P is the possible co-precipitation of toxic ions such as arsenic and fluoride as well as organic contaminants, pathogens or viruses (Mehta et al., 2014) among others. This is highly relevant in terms of the handling of the final product and its suitability for land application. The potential for precipitation using Al and Fe to yield suitable P-bearing soil amendments is limited, since Al can be toxic to many plants at high concentration, especially in acidic soils (Poschenrieder et al., 2008), and P in Al- and Fe-P solids may limit the P solubility to plants and is considered unrecoverable for the purpose of fertiliser production (Donnert and Salecker, 1999; Wendling et al., 2013).

The direct application of dewatered bio-P sludge has been found to be as effective as mineral fertiliser (Erdincler and Seyhan, 2006; Kahiluoto et al., 2015), but similarly, there are increasing concerns over the transfer of chemical and biological contaminants to the environment, affecting food supply (De-Bashan and Bashan, 2004; Krzyzanowski et al., 2014; Yuan et al., 2012). It has been shown that sewage sludge application to soil, although it increases the available nutrient content of the soil, also increases heavy metal concentration in both soil and plant. At a sludge application dose of 20 t/ha or higher, Cd concentrations in rice grain were found to be above the Indian safe limit (Latare et al., 2014). Switzerland has already banned the use of sewage sludge in agriculture (Franz, 2008; Schoumans et al., 2015).

Other issues with the direct application of sewage sludge include the difficulty in its transportation and application, given that sludges are bulky and dense. Dewatering of sludge can reduce haulage costs and removes the necessity for specialist farm equipment, but incurs energy and financial costs (Yuan et al., 2012). The recovery of P from WWTP sludges in purer and more effective forms than that derived directly from sewage sludge is being sought through the approaches outlined in the following subsections, which includes a number of emergent technologies. These approaches are becoming necessary to ensure the safe recovery of P and compliance with current and future legislation.

3.1 Anaerobic digestion and dewatering

Anaerobic digestion (AD) is the process most commonly used for stabilisation of sludge, offering organic solids and pathogen destruction as well as energy recovery in the form of methane (Mehta et al., 2014; Tchobanoglous et al., 2014). AD of bio-P sludges can generate a liquor of approximately 10–50 times higher P concentration than the WWTP influent (Yuan et al., 2012). The majority of the heavy metal load is retained within the sludge, whilst P is

338 released from the biodegradable fractions into the liquid phase. In terms of emerging organic
339 contaminants, it was shown that within AD processes, detected emerging contaminants such
340 as the antidepressant venlafaxine and benzoylecgonine, the main metabolite of cocaine, were
341 preferentially adsorbed and concentrated within the solid material; the majority of the 13
342 compounds detected were not degraded by AD processes (Boix et al., 2016).

343 Concentrations of P in the supernatant of AD processes can vary considerably: 30% of total P
344 has been estimated to be dissolved in the aqueous phase arising from AD of bio-P sludge,
345 whereas <10% is thought to be dissolved after AD of chemical sludges (Petzet and Cornel,
346 2013). This is due to the re-fixation of P into the sludge through precipitation with Fe, Al, Ca
347 and Mg or through adsorption (Petzet and Cornel, 2012). AD of bio-P sludge as a
348 solubilisation technique is a primary step in facilitating the precipitation of struvite in many
349 commercial P recovery processes such as Crystalactor®, NuReSys®, Pearl®, Phosnix® and
350 PHOSPAQ™ (Schoumans et al., 2015). Assimilation of solubilised compounds, in particular
351 emerging organic contaminants, found in AD supernatants into final recovered P products
352 such as struvite may be of particular concern and warrants further investigation.

353 **3.2 Wet chemical extraction**

354 Wet chemical extraction, involving either acid or alkaline dissolution, supports greater
355 solubilisation of P from sludge, sludge ash or other sludge residues, although it can
356 simultaneously solubilise contaminants, of which heavy metals/metalloids are of particular
357 concern. Therefore, the separation of metals and P is highly important when operating wet
358 chemical extraction for P recovery. Additionally, because in recovery through struvite
359 crystallisation, Fe, Al and Ca can compete with Mg to form complexes with orthophosphate,
360 their minimisation leads to improving the efficiency of the recovery process.

Through the acid digestion of various forms of digested sludge, using sulphuric acid (pH 1.8), it has been established that incineration – compared to original, diluted and centrifuged digested sludges – is the better preliminary step for precipitation of struvite. This is because Al, Ca, and Fe could be removed to the greatest extent (98%, 97%, and 80% respectively) (Güney et al., 2008). However, for the effectiveness of P solubilisation, Fe-PO_4-containing raw sewage sludge was more beneficial for the release of P (Sano et al., 2012). Advantages to using alkali extraction as opposed to acid extraction, is that the release of heavy metals/metalloids can be suppressed to lower levels. This may limit the need for filtration technologies, which can be costly and prone to fouling. However, alkali treatment can also reduce the recovery of P to as low as 30% (Mattenberger et al., 2008).

The PHOXNAN (Blöcher et al., 2012) process involves the release and accumulation of P from sludge into a solution suitable for recovery through wet oxidation by the addition of sulphuric acid (pH 1.5). P resides in the resulting solution as H_3PO_4, while the organic content is decreased and other micro-organic pollutants are oxidised. An ultrafiltration membrane separates the remaining solids, a step that is followed by nanofiltration to remove cations. P is accumulated in the final solution mainly as phosphoric acid. In another study, alkaline hydrolysis of excess secondary sludge from an anaerobic/aerobic process was carried out at an optimal pH value of 13, with both P and N being recoverable from the supernatant (Bi et al., 2014). The process enables the release and recovery of 42.0 % PO_4^{3-} (P) and 7.8 % NH_4^+ (N) in the form of struvite. The treatment of sludge with supercritical water gasification was found to release up to 95.5 % P (Acelas et al., 2014). In this case, oxalic acid was reported to have a better performance than sulphuric acid in the leaching of P.

Neither acid nor alkali treatments offer an ideal option for the full solubilisation and recovery of P. The choice of treatment should be considered carefully with respect to the initial accumulation of P in primary and/or secondary treatment. Petzet *et al.* reported that P

386 recovery via wet chemical treatment of sewage sludge ash (SSA) could be optimised by a
387 combination of both acid and alkaline leaching (Petzet et al., 2012). Through an acidic pre-
388 treatment, alkaline insoluble Ca-P fractions are converted to Al-P which can then be easily
389 dissolved through alkaline treatment and separated through the precipitation of Ca-P. The Al
390 fraction can then be reused in chemical precipitation processes in the primary stream. For
391 WWTPs using Al based precipitation and thus generating a high Al SSA, the P-recovery rates
392 were found to be as high as 70–77%. Even where Fe-based precipitation was operated, it was
393 reported that a considerable amount of the required Al is supplied by the decay products of
394 detergent zeolites (Petzet et al., 2012).

395 **3.3 Incineration and P release from sewage sludge ash**

396 The incineration of sludge provides complete oxidation of organic constituents at high
397 temperatures. Mono-incineration, where the sludge is incinerated separately to other wastes,
398 can be a favoured option since it can greatly decrease sludge volume, energy can be
399 recovered and, since phosphate is thermally stable and does not volatilise during the process,
400 P is retained and concentrated in the ash. SSA has been found to contain on average 11.6%
401 P_2O_5 (Cyr et al., 2007) (a form and content comparable to P-rock ores) (Aydin et al., 2010;
402 Weigand et al., 2013). SSA is not generally appropriate for direct application to land
403 however, due to the retention of heavy metals/metalloids and the strong binding of P (Ottosen
404 et al., 2014) due to higher crystallinity of P_2O_5 generated at higher temperatures. In solubility
405 tests with ammonium citrate, one indicator of short-term bioavailability, only 26% of P
406 present in SSA was found bioavailable (Krüger and Adam, 2015). The recovery of P in a
407 purer form may increase the bioavailability of P and reduce the contamination risk.

408 The release of P from SSA can be achieved by the dissolution of the ashes in acid, the
409 separation of heavy metals and the precipitation of calcium phosphate, ferric hydroxide and

aluminium hydroxide, as in the Ash2®Phos process. This process is reportedly economically profitable since it is dealing with a waste which would otherwise incur a cost for disposal and the commercial products produced (mono/di-ammonium-phosphate and Fe and Al precipitants) (EasyMining-Sweden, 2017). P content (>95%) from SSA was recovered by acidification with HCl (Xu et al., 2012). Heavy metals were subsequently removed from solution using a cation exchange resin. P was recovered in the form of struvite (97% pure), which has high P bioavailability of 94% and low metal content, thus comparable to a high quality fertiliser. Electrodialysis was also studied as an option for the separation of heavy metals/metalloids and P after pre-treatment with sulphuric acid. The process separated P from heavy metals/metalloids effectively with up to 70% mobilisation of the P from the SSA (Guedes et al., 2014).

421 **Table 2.** Examples of commercial processes for P recovery and the form of the final P product derived.

422

Process	Information and process description	Final product	Reference
AirPrex® process	Crystallisation of struvite applied directly in the digested sludge stream. CO_2 is stripped to increase pH. $MgCl_2$ is added. AirPrex® systems are currently operational at several WWTPs in Germany and The Netherlands. The world's largest AirPrex® system is being constructed at the WWTP of Amsterdam. Developed by Berliner Wasserbetriebe (Germany).	Struvite	(Eliquo Water & Energy BV, 2016; Tchobanoglous et al., 2014)
DHV Crystalactor®	The sludge side stream is fed into the reactor and recirculated. Quartz sand is initially added as seed material to accelerate precipitation. Pellets settle to the bottom. Developed by DHV (NL).	Struvite, Mg-P or Ca-P	(Giesen, 2016; Tchobanoglous et al., 2014)
NuReSys® process	Air is initially added and CO_2 is stripped from the side stream followed by $MgCl_2$ addition in the stirred crystalliser tank where struvite forms pellets. NaOH is added to maintain pH in the range 8.1-8.3. Pellet size can be controlled by stirring speed. Developed by Akwadok/NuReSys (Belgium).	Struvite	(NuReSys, 2016; Tchobanoglous et al., 2014)
Ostara Pearl® process	Struvite crystallisation is achieved through treatment of sludge side stream in a fluidised bed crystalliser. Effluent is recirculated and $MgCl_2$ and NaOH are added as the Mg source and for pH maintenance respectively. Developed at the University of British Columbia and introduced at full-scale by Ostara Nutrients Recovery Technologies Inc. (USA).	Struvite (Crystal Green®)	(Ostara, 2016; Tchobanoglous et al., 2014)
Phosnix® process	A cylindrical reaction zone with a conical bottom section is applied. $Mg(OH)_2$ and NaOH added as a source of Mg and for the control of pH respectively, and aerated to strip CO_2. Struvite settles to the bottom where it is removed with the effluent recirculated. Developed by Unitika Ltd (Japan).	Struvite	(Katsuura, 1998; Tchobanoglous et al., 2014)
PHOSPAQ™ process	A side stream process consisting within an aerated zone. Air lift is designed to provide mixing, strip CO_2 and increase pH, and provide DO for biological treatment. MgO is used as the Mg source for the precipitation of struvite. Developed by Paques (The Netherlands).	Struvite	(PAQUES, 2016; Tchobanoglous et al., 2014)

FIX-Phos	Calcium silicate hydrate (CSH) particles are added into the anaerobic digester. The CSH adsorbs P as Ca-P and controls struvite formation by reducing the P concentration in the digestate. The Ca-P on CSH can be separated and recovered from the digested sludge.	Ca-P on CSH	(Petzet and Cornel, 2012)
P-RoC®	P recovery from waste water similar to the Crystalactor® process however complex pre-treatment steps such as pH adjustment or CO_2 stripping can reportedly be avoided. Crystallisation products showed a P content of 11 % to 13 % which was comparable to phosphate rock.	Ca-P on CSH	(Berg et al., 2001)
PHOXNAN	The process combines low pressure wet oxidation with two membrane filtration steps. High temperature and pressure at acidic conditions (sulphuric acid added to adjust pH to 1.5) are used for sludge oxidation with pure oxygen. Organic components are decreased and organic pollutants are oxidised. Due to the low pH, P exists in solution mainly as H_3PO_4 and H_2PO_4. The first membrane uses ultrafiltration to separate solids, the second membrane uses nanofiltration to eliminate metal ions.	H_3PO_4	(Blöcher et al., 2012)
Aqua Reci	Commercially, the process makes use of supercritical water oxidation. Leaching is accomplished with a base, which selectively dissolves P. By addition of calcium, P can be precipitated.	Ca-P	(Levlin, 2007; Stendahl and Jäfverström, 2004)
EcoPhos®	HCl or H_2SO_4 is used for the digestion of any phosphate raw material including P-rock or SSA. The EcoPhos® process involves the treatment of the obtained slurry to remove dissolved impurities and solid residues and produces a phosphate product such as dicalcium phosphate or H_3PO_4.	DCP or H_3PO_4	(DeRuiter, 2014; Ecophos, 2017)
Mephrec	The process utilises temperatures of up to 2000 °C where the sewage sludge melts under the addition of oxygen, with all organic pollutants destroyed. The metals obtained can be recycled, the slag is a form of fertilizer with high plant availability, free of heavy metals/metalloids and organic pollutants – similar to Thomas phosphate fertiliser (a P-rich slag produced in the steel industry).	Detoxified mineral P	(Nuremberg GmbH, 2016)
AshDec	Ash and natural earth alkali salts are exposed to a temperature of 1 000-1050°C. The heavy metals/metalloids react with the salts, become gaseous and evaporate. The phosphate compounds are transformed into plant available species.	Detoxified mineral P	(Outotec, 2017)

423

4 Recovered P products from treated sludge

P recovery processes from sewage sludge, including commercial and large scale approaches and the characteristics of the final products obtained are detailed in Table 2. Recent description and comparison of commercial approaches for P recovery from municipal wastewater is provided in detail elsewhere (Egle et al., 2016, 2015). Current EU fertiliser regulation recognises only primary mineral-derived P products as fertiliser whereas the rest of these recovered P products cannot yet be labelled as such (European Union, 2003) – the legislation however is currently under revision to include recovered P residues such as struvite, ashes and pyrolysis materials (European Commission, 2016; Huygens et al., 2017). This revision also limits the composition of fertiliser products in terms of impurities and level and bioavailability of nutrients, therefore selective routes to obtain these products will be beneficial. Among the recovered products in Table 2, struvite stands out due to its usability directly as a slow release fertiliser (Bouropoulos and Koutsoukos, 2000).

4.1 Struvite

Struvite precipitation has been the main focus for P recovery commercially, and is widely recommended for treatment of sludge digester liquors in large WWTPs operating EBPR processes (Martí et al., 2010). Struvite crystallises as hard crystalline deposits when a molar ratio and concentration of $Mg:NH_4:PO_4$ exists of 1:1:1 and exceeds the product solubility constant, respectively (Crutchik and Garrido, 2016). For crystallisation to occur readily, a concentration between 100 and 200 mg PO_4^{3-}/L is required (Rittmann et al., 2011), which tends to be at least 10 times higher than typically found in the liquid phases of municipal wastewater treatment. The crystallisation of struvite and other P-rich precipitates results in a very low degree of impurities. This is advantageous because the selectivity of this process

447 leads to a safe product that can be applied to soil directly, despite the possible presence of
448 heavy metals and other contaminants in the EPBR effluents. Solution pH can be increased by
449 the addition of a base or through CO_2 stripping (Petzet and Cornel, 2013); struvite becomes
450 highly insoluble at alkaline pH and therefore increasing solution pH can lead to increased and
451 accelerated struvite formation (Ariyanto et al., 2014). The effective precipitation of struvite
452 has been shown feasible in the treatment of side streams originating from the digestion of
453 EBPR sludge (Mattenberger et al., 2008). Practically and economically, however, struvite
454 production is currently viable only in large WWTPs where enhanced biological accumulation
455 of P can be applied.

456 The precipitation of struvite is usually initiated with the addition of a Mg source as most
457 municipal wastewaters contain more N and P than Mg (Rahman et al., 2014), however some
458 streams can require PO_4^{3-} additions where the P content is low. The source of Mg used may
459 contribute up to 75% of the overall production costs of struvite (Dockhorn, 2009), however if
460 P is accumulated using EBPR then Mg may be the only chemical requirement in the WWTP
461 process. The most common source of additional Mg is $MgCl_2$ or MgO, though many other
462 materials have been used experimentally. Lahav *et al.* (2013) investigated using concentrate
463 from seawater nanofiltration as a cheap Mg (II) source for precipitating struvite from
464 municipal sludge centrifuge wastewater. Wood ash and bittern salts have also been found to
465 be good sources of Mg in struvite crystallisation processes (Lee et al., 2003; Sakthivel et al.,
466 2012).

467 Where chemical precipitation is operated, Fe or Al may be present at high concentrations. P
468 may consequently co-precipitate during solubilisation in AD or other WWTP processes. A
469 stream of sufficiently concentrated P may then not be available to support effective struvite
470 precipitation and ensure high rates of P recovery. High Ca^{2+}/PO_4^{3-} ratios have been found to

471 be detrimental to struvite formation in pilot- and full-scale plants treating potato and dairy
472 wastewater, respectively (Moerman et al., 2009).

473 Uncontrolled precipitation of struvite can occur within centrifuges, digesters and sludge
474 liquor pipes (Petzet and Cornel, 2012). Where the controlled precipitation of struvite is
475 carried out in side stream processes, after the dewatering of the digested sludge, this
476 undesired precipitation can make the processes less efficient with potential additional costs
477 being incurred from the maintenance of equipment. The commercial Airprex® process (Table
478 2) precipitates struvite directly in the sludge stream and can therefore have economic benefits
479 regarding scaling of pipes and sludge dewatering equipment. The recovery of the struvite
480 then depends on the subsequent separation of digested sludge. Waternet, Amsterdam, which
481 recovers P as struvite from bio-P sludge using the Airprex® process, reportedly makes an
482 annual saving of €500 000 due to improved dewatering and reduced scaling problems – the
483 recovered struvite product is sold to the fertiliser industry for between €50–100/t for fertiliser
484 production (Waternet, 2017). For the use of struvite in agriculture it is important to minimise
485 contaminants, for example heavy metals and metalloids may become incorporated into the
486 precipitated struvite. Arsenic, for example, has been found sequestered into a synthetic
487 struvite at concentrations of up to 547±15 mg/kg (Lin et al., 2013). This potentially renders
488 struvite recovered from some waste streams unusable in agriculture without removal of heavy
489 metals/metalloids.

490 Struvite has an economic value as an effective slow release fertiliser, for example it was sold
491 in Japan at a USD value of $250 per tonne in 2001 (Forrest et al., 2008; Ueno and Fujii,
492 2001). Other than in municipal WWTPs, struvite precipitation has recently been investigated
493 in a broad variety of wastewater streams from bakery production (Uysal et al., 2014); the
494 semiconductor industry (Warmadewanthi and Liu, 2009); swine and poultry farming (Jordaan
495 et al., 2010; Taddeo and Lepisto, 2015; Yang et al., 2012); slaughterhouse wastewater

(Kabdaşli et al., 2009); landfill leachate (Huang et al., 2014); human urine (Lind et al., 2000) and within the potato processing industry (Uysal and Kuru, 2013). Some studies have been found effective, in precipitating struvite from agro-industrial wastewaters, at pilot- and full-scale (Moerman et al., 2009), whereas largely, studies still remain to be proven effective at full-scales.

4.2 Ca-P precipitates

P content in recovered Ca-P products can vary from 12–20% and can be assumed to have a higher solubility than that of well-crystallised Ca-P (Cabeza et al., 2011). From a commercial viewpoint, however, the recovery of P in the form of Ca-P is beneficial since it has more diverse applications in industry than struvite (Okano et al., 2013). Calcium phosphate (mainly as hydroxyapatite, $Ca_5(PO_4)_3OH$) reflects the composition of rock phosphate and should be easily adopted as a secondary P source in existing industry and infrastructure (Song et al., 2006; Tervahauta et al., 2014). Indeed, many established commercial processes already derive Ca-P precipitates as the final product (Table 2).

Hydroxyapatite is the most common form of Ca-P precipitate and forms at high pH, typically >10 (Rittmann et al., 2011). At lower pH, dicalcium phosphate dihydrate ($CaHPO_4\,2H_2O$) and octacalcium phosphate ($Ca_8H_2(PO_4)_6\,.5H_2O$) are expected to be the more stable phases. However, these precipitated phases are thought to transform into the more thermodynamically stable hydroxyapatite over time (Desmidt et al., 2015; Seckler et al., 1996).

Calcium silicate hydrates (CSHs) have been studied as a seed for Ca-P precipitates. Amorphous CSHs (Okano et al., 2013) and tobermorite-rich waste materials from the construction industry (P-RoC) (Berg et al., 2001) have been investigated. Other calcium rich materials investigated include cattle bone (Jang and Kang, 2002). In the precipitation of Ca-P,

bicarbonate alkalinity often requires control as competition between hydroxyapatite and calcium carbonate precipitation can occur. This is often provided through the removal of carbonates by acidification and CO_2 stripping, but the addition of a base such as NaOH to increase pH can increase the cost of the process. It has been noted, however, that using CSH as a seed material avoids the need to modify the influent and that removal of carbonate was unnecessary, with phosphate and carbonate co-precipitated to the solid surface (Song et al., 2006).

Commercial processes based on Ca-P precipitation include *FIX-Phos,* in which Ca-P is directly precipitated (on CSH) into sludge. This holds the same risks identified for the corresponding struvite process (see section 4.1).

4.3 Thermochemically treated sewage sludge ash

Thermochemical treatment is an option for deriving a metal-depleted solid with higher bioavailable P. After mono-incineration, the addition of Mg and Ca chlorinated salts and water, thermochemical treatment at approximately 1000°C was found to increase P-bioavailability due to the formation of Mg- and Ca- bearing phosphates such as chlorapatite, farringtonite and stanfieldite (Adam et al., 2009). Heavy metals/metalloids are depleted mainly due to their volatilisation as heavy metal chlorides. The legal limits of Fertilizer Ordinance in the EU were reportedly met in most cases. KCl added to SSA favoured Cu removal over Zn, but the converse was the case for $MgCl_2$ (Mattenberger et al., 2008). This has relevance to the thermochemical treatment of incinerated biological sludges since they tend to contain higher concentrations of Cu and Zn (Franz, 2008). In most cases Cd, Cu, Zn and Pb can be removed up to at least 90 wt% from SSA. However, even with higher Cl addition at the same incineration temperatures (1000°C), Cr and Ni have been found to have low volatility (Fraissler et al., 2009; Vogel and Adam, 2011).

Two commercial processes in the literature, AshDec and Mephrec, offer recovered products in the form of mineral-P from thermochemical SSA treatment. The AshDec process is a calcination process based on fluidised bed technology (Outotec, 2017). The Mephrec process, through metallurgic treatment at high temperature, provides a slag that contains P of high plant availability, free from heavy metals/metalloids and organic pollutants, and similar in form to Thomas-phosphate fertiliser. This is used by the fertiliser industry after further processing but can be safely used in organic farming (Nuremberg GmbH, 2016).

5 Experimental P recovery through sorption processes

Several experimental technologies are being developed that have shown high efficiency for P recovery at bench or small pilot scale: membrane filtration (Gerardo et al., 2015; Qiu and Ting, 2014), electrodialysis (Zhang et al., 2013), and nanoparticle-based sorbents (Lu et al., 2015; Su et al., 2015; Tu and You, 2014) as well as various modified mineral- and biological-based sorbents (Chiou et al., 2015; C. Fang et al., 2015; Nguyen et al., 2014b; Yu et al., 2015). However, cost and practicality have so far prevented these technologies from being adopted in commercial scale operations.

Sorption techniques have been shown to have potential for removal of a wide range of contaminants from dilute wastewater effluents (Busquets et al., 2014; Nguyen et al., 2013; Sivasankar et al., 2013). The use of easily obtainable or synthesisable materials as well as waste materials may reduce the need for more expensive chemical additives or modification to existing WWTP infrastructures. As well as encouraging the precipitation of P by seeding, mentioned in preceding sections, sorbent-based processes can include other coexisting mechanisms such as ion exchange, ligand exchange, and electrostatic interactions to directly sorb P from the waste stream. Such processes can potentially fit into existing WWTP infrastructures and provide enhanced P removal and recovery. Sorbents have not been widely

568 employed in WWTPs as stand-alone P recovery processes. Similarly, the potential of
569 recovered sorbed-P fertiliser or soil amendment has not been widely considered or assessed.
570 However, a wide variety of materials evaluated for the sorption of P have shown high
571 potential, these have been compiled in Table 3.

572 An extensive review of agricultural by-products and wastes for the sorptive removal and
573 recovery of P recently concluded that organic materials require some form of pre-treatment
574 before use in P recovery, due to the lack of anion binding sites (Nguyen et al., 2014a).
575 Surface modifications can significantly enhance the capture efficiency, but poor reusability of
576 materials recycled from agriculture has been reported. Capture and recovery of P by biochars
577 has been investigated and modification of the feedstock, mainly through incorporation of Fe
578 or Mg, has been shown to be necessary to enable efficient uptake of P (Shepherd et al., 2016;
579 Yao et al., 2013). Although the application of P-bearing biochar to soil has been suggested,
580 the technology is still in its infancy. While efficient P removal can be brought about through
581 material modifications, the added cost to the process may make their application to soil
582 uneconomic. Among the potential mineral sorbents zeolitised fly ash, layered double
583 hydroxide (LDH) minerals and Li-intercalated gibbsite have exhibited high potential for P
584 sorption from solution (Wendling et al., 2013). Their subsequent direct use as nutrient
585 bearing soil amendments or as P fertiliser has been suggested, but not yet demonstrated.

586 **Table 3.** Sorbent materials used for the uptake of P: Sorption capacities, application and mechanisms.

Sorbent material	Sorption capacity/ efficiency	Information about study/ experiment	Reference
Powdered sulphate-coated zeolite	111.5mg P/g	Three novel composite adsorbents, sulphate- coated zeolite (SCZ), hydrotalcite (SCH) and activated alumina (SCAA). Sulphate coating improved sorption capacity in the case of SCZ and SCAA. Adsorption thought to have occurred fast. Main mechanism: ion-exchange between phosphate and sulphate on the surface of the adsorbents.	(Choi et al., 2012)
Powdered hydrotalcite	26.1 mg P/g		
Sulphate coated activated alumina	49.7 mg P/g		
Lanthanum hydroxide	107.5 mg P/g	Surface area 153.3 m^2/g. Performed well across a wide range of pH values. Main mechanism: ligand exchange.	(Xie et al., 2014)
Cerium-zirconium binary oxide nanoparticles	36.6 mg P/g	Ce/Zr binary oxide nanoparticles were synthesised with different structure, crystal size, surface properties, and phosphate adsorption performance. Main mechanism: inner-sphere complexing mechanisms were thought to dominate, the surface -OH groups playing a major role.	(Su et al., 2015)
Cement based materials	30.0 mg P/g	High Si, Ca, Al and Fe content within cement materials. Main mechanism: precipitation with Ca predominantly.	(Wang et al., 2014)
Zirconium loaded okara	14.4 mg P/g	The phosphate removal was rapid, reaching 95% in 30 min from an initial concentration of 5 mg P/L. Adsorption tested between 10 – 500 mg P/L.	(Nguyen et al., 2014b)
Magnetic Fe-Zr binary oxide	13.7 mg P/g	Incorporation of Fe into Fe-Zr oxide allows for magnetic recovery. Zr oxide was a suitable adsorbent for P. Main mechanism: ion-exchange of Zr species and partly originated from magnetite species of Fe–Zr binary oxide.	(Long et al., 2011)
Scallop shell synthesized ceramic biomaterials	13.6 mg P/g	Scallop shells, montmorillonite and starch (1:1:1) were mixed to a paste. The ceramic samples were dried at 105°C for 24 h in an oven and calcined at 600°C. A surface area of 53.74 m^2/g was reported.	(Chen et al., 2013)

Nano bimetal ferrites (CuFe2O4 – Green synthesis)	13.5 mg P/g	Manufactured from industrial sludge. Fast sorption rate within first 10mins reached equilibrium within 120mins. Magnetic. Large potential for desorption and recovery. Main mechanism: inner-sphere mechanisms.	(Tu and You, 2014)
Amine-functionalized silica magnetite	>~13 mg P/g	A magnetic adsorbent: amine-functionalized silica magnetite. The maximum adsorption was found to occur at pH 3.0.	(Chiou et al., 2015)
Zirconium loaded bifunctional fibers (fibrous ligand exchange adsorbent)	Breakthrough point at ~340BV	Adsorbent slightly preferred phosphate to arsenate. Sorbent reversible and suitable for multiple reuse cycles. Main mechanism: ligand exchange – sorption slightly enhanced due to co-ion and Donnan invasion mechanisms (Cl^- and SO_4^{2-}).	(Awual et al., 2014)
Nano-sized iron oxide coated sand	69.1% P removal without magnetic field application, 75% with.	20mL/min flow rate through column of 20cm height, 5cm width. Main mechanism: precipitation of Fe-P deposits on the surface of sand.	(Khiadani Hajian et al., 2013)
Chemically surface-modified silica filter	Effective up to 1.5L of influent with 36 filters (900g) to remove to P to below 1 mg/L. 20 seconds per 500mL with 36 filters.	Glass modified silica granules packed into 25g porous cylindrical filters. After regeneration, filters (36) unable to reduce P concentration to below 2 mg/L. Main mechanism: ion-exchange.	(Kim et al., 2012)

587

588 Using sorbent materials for the removal and recovery of P for subsequent direct use as a
589 fertiliser or soil amendment is attractive, provided that the sorbent material is economic and
590 has adequate P affinity without retention of contaminants. If modifications are required to
591 provide these, the cost and complexity of additional processing have to be considered. Rather
592 few materials shown to be effective as sorbents for P are also suitable for direct application to
593 agricultural land. Waste materials are an attractive option for having a low (or no) price and
594 for their often wide availability, but incur the cost of compliance with regulation (European
595 Union, 2003). Variability in composition is a further challenge. Also, materials showing high
596 affinity for P in sorption studies may also have minimal potential for P release. Effective
597 sorption is often brought about by high Fe or Al contents which, as discussed, may then limit
598 solubilisation of P within the soil, or may be toxic in surrounding aquatic environments.

599 Other issues regarding the sorption of P from wastewaters is the co-sorption of toxic
600 compounds that contain heavy metals/metalloids, or metals that compete with phosphate and
601 other anions for sorption sites; selective recovery of P should therefore be a key goal of any
602 recovery process. A Zn-Al LDH material reported in the literature provides an example for
603 such selectivity. Intercalated with pyromellitic acid this sorbent achieved 97.4% selectivity
604 toward P at pH 7 from complex solutions containing $H_2PO_4^-$, SO_4^{2-}, CO_3^{2-}, NO_3^- and Cl^- (Yu
605 et al., 2015). Although this material showed a selective and effective P sorption compared to
606 other options, the practicality of the material in terms of recyclability, usability or cost was
607 not discussed. For innovation in sorbent technologies to translate to WWTP use, their
608 potential feasibility should be assessed and demonstrated at an early stage. Their efficiency at
609 low or high P concentrations should be assessed in relation to their suggested use; as filtration
610 media in a tertiary process in the primary stream or for sorption of P within a side stream
611 process treating sludge liquors and dewatered sludge, respectively. But their end use is an
612 equally important consideration in developing sorbents for P recovery – the effective

bioavailability of P and its re-release into soil when used as a fertiliser or P-bearing soil amendment, or its potential for regeneration, i.e. re-use after desorption of P and its separate recovery. Sorption of P remains a flexible, efficient and potentially effective option; either as a potentially lower-cost alternative to crystallisation technologies, or as an additional technology that provides for enhanced P removal and recovery potential.

6 Bioavailability of recovered P products

Not all P in soil is bioavailable to plants and P is a key limiting nutrient in terrestrial ecosystems (Elser, 2012; Maltais-Landry et al., 2014). Phosphorus therefore plays a critical role in productive agriculture (Withers et al., 2014), but its plant availability however can often be low: it forms sparingly soluble fractions due to adsorption, precipitation or conversion to organic fractions in soil (Werner and Prietzel, 2015), via geochemical processes that depend on several soil properties such as the abundance of Ca, Al and Fe oxides, pH and organic matter content. The bioavailability of P in recycled P products can be assessed using chemical analogues for plant acquisition (i.e. using extractants) or more directly in pot or field trials. For P to be utilised by plants it must be soluble or solubilised, but solubility and potential bioavailability depends on a number of soil-related factors, so its assessment as an effective and suitable fertiliser should be undertaken in diverse environments. The use of Ca and Mg in crystallisation processes has been shown to have high potential for P recovery, owing to the solubility of precipitated Ca and Mg products in soil. The bioavailability of struvite has been more widely investigated: i.e. through cultivation of Chinese cabbage (Ryu et al., 2012); maize (Liu et al., 2011); maize and tomato plants (Uysal et al., 2014); corn and tomato plants (Uysal and Kuru, 2013). Struvite-P has been found to be relatively soluble and bioavailable across a wide range of pH conditions and soil types. Recovered Ca-P products have been investigated to a lesser extent.

637 Struvite can be considered as the better product compared with Ca-P, in terms of
638 bioavailability. Through isotopic labelling techniques with ^{33}P, a reference hydroxyapatite
639 and a recovered product partly composed of hydroxyapatite, were found to be less effective,
640 in terms of the plant availability of P, than triple super phosphate (TSP), reference struvite
641 and a recovered product composed of both struvite and hydroxyapatite (Achat et al., 2014a).
642 However, using the same recovered products in pot and soil incubation experiments with
643 slightly acidic soil growing ryegrass and fescue, both were as effective as TSP and the
644 struvite reference material (Achat et al., 2014b). When the plant uptake of P derived from the
645 applied products was compared with that derived from the TSP, the reference hydroxyapatite
646 was found to have only 22% relative effectiveness, compared with 85-96% for the recycled
647 products and 111% for the reference struvite. This was likely due to higher solubility of
648 poorly crystallised phases of Ca-P associated with the recycled products (Achat et al., 2014b).
649 The recovered P products containing struvite and Ca-P were derived from pig manures and
650 dairy effluents.

651 The bioavailability of various recycled P products has also been compared with TSP and P-
652 rock in pot experiments with maize in two contrasting soil environments (pH ($CaCl_2$) 4.7 and
653 6.6) over a period of 2 years. Recycled struvite products were found to be as effective as TSP
654 in both soils, but the Ca-P product was only effective in the acidic soil (Cabeza et al., 2011).
655 The restricted effectiveness of Ca-P to acidic soils is due to the enhanced disintegration of the
656 P-rich material in higher H^+ concentrations and its relative stability in alkaline conditions.
657 Similarly, an alkali sinter phosphate made from meat and bone meal was as effective as TSP
658 in the acidic soil, while a cupola furnace slag was in the neutral soil (Cabeza et al., 2011).
659 Both the SSA and a meat and bone meal ash had low effectiveness, in terms of P uptake and
660 P concentration in the soil solution, and were comparable to rock-P. It was concluded that P
661 products obtained through chemical processes were suitable for direct application as

662 fertilisers, especially struvite, and the ash products could be potential raw materials for P
663 fertiliser production (Cabeza et al., 2011).

664 The thermochemical treatment of SSA is a promising technology in deriving heavy metal
665 depleted residues containing P in bioavailable forms. Two SSA products thermochemically
666 treated with either $MgCl_2$ or $CaCl_2$ were investigated for their plant availability in pot trials
667 with ryegrass using ^{33}P (Nanzer et al., 2014). The shoot uptake of P from the Mg treated SSA
668 was found to be higher than the Ca treated SSA (15.7 and 8.3 mg P/kg acidic soil,
669 respectively). The effectiveness of the Mg treated SSA relative to a water-soluble P fertiliser
670 was 88% in an acidic soil, 71.2% in a neutral soil but was reduced to 4% in an alkaline soil
671 (Nanzer et al., 2014).

672 Large gaps still remain in the understanding of the release and plant availability of P in soils
673 from recovered products derived from WWTPs. From review, the use of indirect isotopic
674 labelling techniques would appear to be the best method in assessing the contribution of
675 recovered-P to plant available P in soil and P utilised by the plant. Further investigation and
676 empirical information regarding the availability, plant uptake and cycling of P in soils related
677 to the application of recovered products and residues will lead to a greater understanding and
678 confidence in their use as alternatives to inorganic-P derived fertilisers. It is additionally
679 important that both the removal process and reuse of P are considered on a case-by-case basis
680 – not all recovery processes will be applicable to all wastewaters, and similarly not all
681 recovered products will be equally effective across different soil environments. As sorbent
682 materials can be derived from a wide variety of materials and processes, providing a myriad
683 of physical and chemical characteristics, P sorbed to and within the surface and structure of
684 these solids may have wide ranging applications.

7 Conclusions

The diminishing quantity and quality of P-rock reserves, and the eutrophication of water bodies, are instigating a critical need to recover P from WWTPs in forms suitable for agricultural application. There are numerous recovery options that vary in application (i.e. sludge, sludge liquor, primary stream, SSA) and technology used (precipitation, EBPR, AD, wet chemical extraction, thermochemical treatment). The chemical precipitation of struvite and Ca-P, from the digested EBPR sludge stream, are the favoured routes that are technologically well developed and already in operation in a number of WWTPs. The mono-incineration of sludge followed by thermochemical treatment of the SSAs are also promising steps in the production of secondary P residues suitable as a detoxified P fertiliser.

EBPR currently forms the basis of chemical crystallisation technologies in providing a process stream of suitable concentration for efficient P recovery. The minimisation of Fe and Al, especially where P is to be recovered from anaerobic digestate, is important to maximise P release. Where chemical accumulation processes are required to be operated due to spatial, economic or infrastructural requirements the metal salt applied and the resulting sludge composition should be considered regarding the suitability of the sludge residue for processing by the fertiliser industry or its use directly as a detoxified residue after thermochemical treatment.

Technologies such as thermochemical treatment, wet chemical extraction and electrodialysis may be used to increase the total recovery potential to around 90%, and in some cases, have been shown to be economically feasible. However, the present cost of some existing and novel technologies is not yet offset by a marketable product due the current omission of recovered products from fertiliser legislation. Where P must be removed on in some cases recovered, to comply with statutory limits and regulation, a range of approaches will be

valuable and necessary despite not being profitable – the inclusion of recovered P products such as struvite and ashes in to the revised fertiliser legislation will then create a value and a market for these products. This is important in enabling recovered-P products to substitute and compete with primary fertilisers on the market and could foreseeably require subsidisation or regulatory forcing until an increase in price of primary fertilisers ensures that widespread agricultural adoption is economical.

Around 90% of the incoming P load can be incorporated into sewage sludge, however to consistently achieve P limits of <1 mg/L, WWTPs require a further removal of P before discharge, with future legislation foreseeably requiring increasingly lower concentrations of P in discharge. Consequently, a gap in wastewater treatment strategy has presented itself; the "polishing" of effluents, other than by additional chemical dosing, in a tertiary treatment setting where EBPR may not be able to reliably meet required concentrations. Experimental technologies (ion-exchange, novel sorption processes, membrane filtration, etc.), although not yet commercially operational, may become key in providing an enhanced P removal and recovery potential. Sorbents, if effective, may easily be incorporated into existing infrastructures and may provide alternatives to technologies unachievable at smaller WWTPs – currently the precipitation of struvite/ Ca-P can only be practically applied at large WWTPs operating EBPR. The focus of experimental technologies and especially sorption processes is deriving recovered-P products or residues of suitable purity, form, economy and bioavailability for their safe and effective application as fertiliser to agricultural land.

Struvite compares well to TSP and other mineral-P fertilisers in pot trials under a range of soil pH values, but full field trials and longer term tests are still lacking. The application of recovered-P products and residues to soils and their use by crops needs further investigation and empirical information – understanding the bioavailability and availability of recovered P and its use by plants in a wide range of soils and environments is important to increase

734 confidence in the precise and effective use of these products as a substitute for conventional
735 inorganic-P derived fertilisers. This will be vital for the widespread recovery of P and the
736 adoption of recovered-P as fertiliser.

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Highlights

- P recovery is a pressing issue and wastewater provides a substantial opportunity
- Struvite/Ca-P crystallisation is limited to <25% P recovery of the influent P load
- Crystallisation, thermo- and wet-chemical processes are being commercially applied
- Revised fertiliser legislation and P limits drives wider adoption of technologies
- All approaches should focus on obtaining agriculturally effective forms of P

Trends in the recovery of phosphorus in bioavailable forms from wastewater

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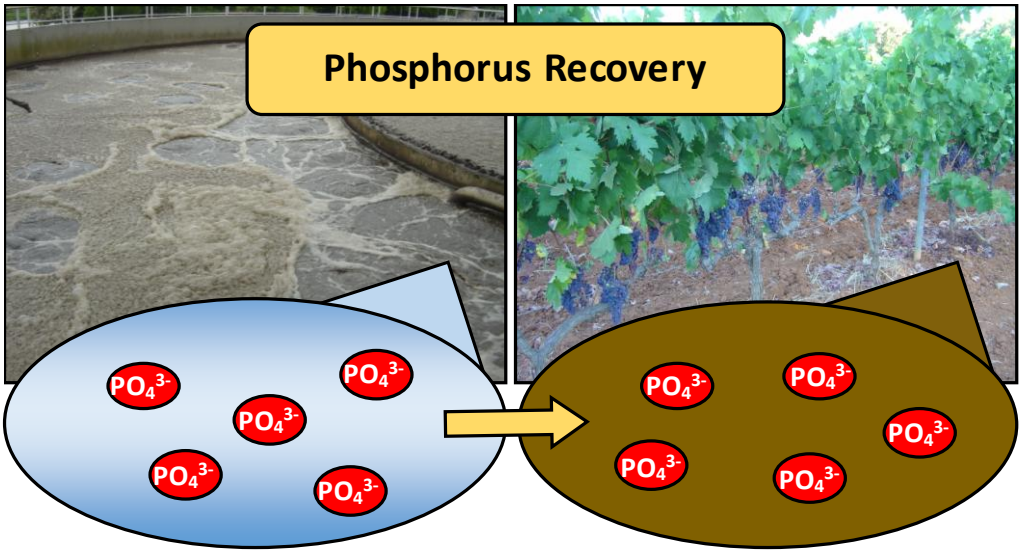
Abstract

Addressing food security issues arising from phosphorus (P) scarcity is described as one of the greatest global challenges of the 21st Century. Dependence on inorganic phosphate fertilisers derived from limited geological sources of P creates an urgent need to recover P from wastes and treated waters, in safe forms that are also effective agriculturally – the established process of P removal by chemical precipitation using Fe or Al salts, is effective for P removal but leads to residues with limited bioavailability and contamination concerns. One of the greatest opportunities for P recovery is at wastewater treatment plants (WWTPs) where the crystallisation of struvite and Ca-P from enhanced biological P removal (EBPR) sludge is well developed and already shown to be economically and operationally feasible in some WWTPs. However, recovery through this approach is limited to <25% efficiency unless chemical extraction is applied. Thermochemical treatment of sludge ash produces detoxified residues that are currently utilised by the fertiliser industry; wet chemical extraction can be economically feasible in recovering P and other by-products. The bioavailability of recovered P depends on soil pH as well as the P-rich material in question. Struvite is a superior recovered P product in terms of plant availability, while use of Ca-P and thermochemically treated sewage sludge ash is limited to acidic soils. These technologies, in addition to others less developed, will be commercially pushed forward by revised fertiliser legislation and foreseeable legislative limits for WWTPs to achieve discharges of <1 mg P/L.

Keywords:

Phosphorus recovery; wastewater; sewage sludge; struvite; sorption; bioavailability.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1 Introduction

Phosphorus (P) is an essential plant nutrient and makes up around 0.2% of plant dry weight (Jiang and Yuan, 2015; Schachtman et al., 1998). In aquatic ecosystems, low concentrations of P benefit the biological productivity of freshwater lakes, reservoirs and rivers. Concentrations of just ~0.02 mg P/L can be considered to cause eutrophication (Correll, 1998), having negative ecological effects where promoted algal growth (Yao et al., 2013) can cause hypoxia and negative effects from algal toxins (Bláha et al., 2009; Žegura et al., 2011).

Negative impacts within ecosystems caused by an excess of P has led governments to limit the P concentration in waters. As a whole, the Water Framework Directive 2000/60/EC (European Commission, 2008) in conjunction with the Council Directive 91/271/EEC concerning urban wastewater treatment (European Commission, 1991), identify sensitive areas where high levels of P would have large ecological impacts – and enforce the control of P in wastewater discharges, respectively. As an annual average, it is required that P concentrations within wastewater effluents are below 1–2 mg P/L, depending upon the sensitivity of the receiving environment and the size of the wastewater treatment plant (WWTP), or are reduced by 80% from the influent concentration (European Commission, 1998, 1991). Austria, Germany and Switzerland have now made P recovery mandatory from municipal sewage sludge (European Sustainable Phosphorus Platform, 2017).

The P loading within many ecosystems is a result of P discharges from WWTPs or the use of P in agriculture. Figure 1 summarises key P flows and losses throughout the global agricultural production and food consumption system. The inorganic P cycle is extremely inefficient and wasteful. Losses of P to natural water bodies from wastewater discharge represents approximately 10 % of inorganic P derived fertiliser applied to arable soil globally (see “A” in Figure 1). These losses create both a need and an opportunity, with respect to P

recovery and re-use, needed not only to ensure good ecological status of waterways, but also to maintain the global productivity of agriculture.

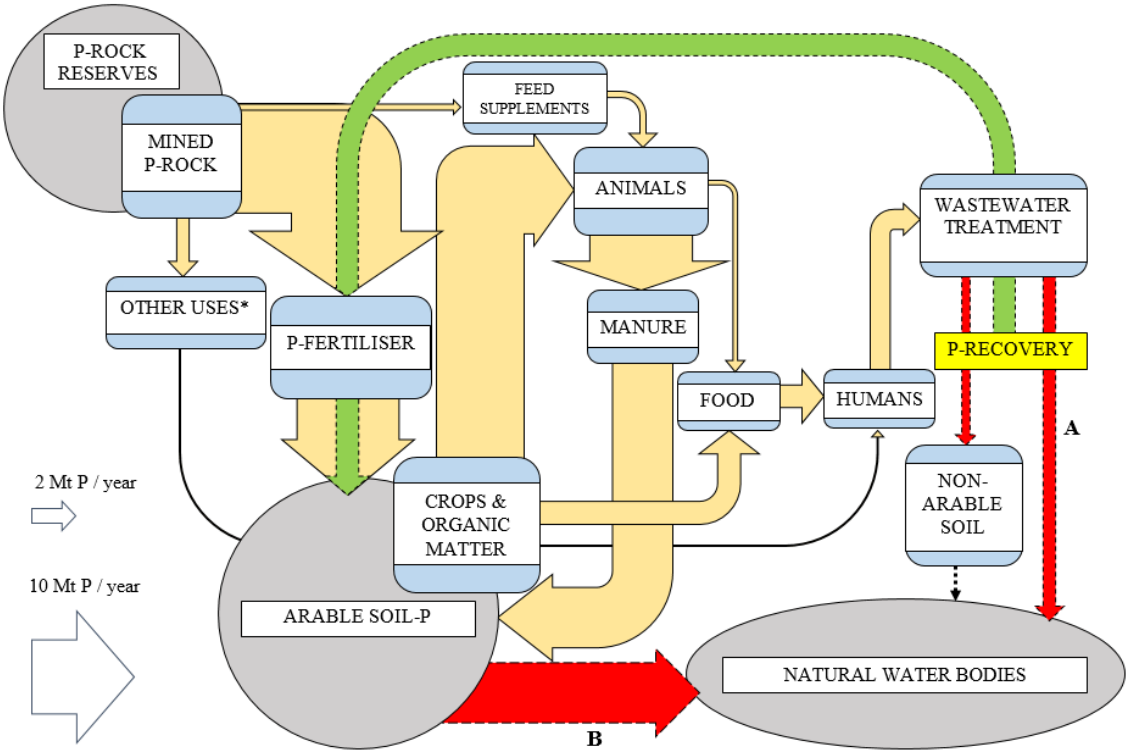

Figure 1. Diagram of key P flows. The widths of the arrows semiquantitatively represents figures reported by Cordell et al. (2009) in million tonnes (Mt) of P per year. Yellow, red and green arrows represent flows of P between major points of use in the food production and consumption system; key P losses and the potential flow of recovered-P from WWTPs, respectively. Losses such as those arising from fertiliser production and distribution, agricultural residues, and food chain losses are not shown. The blue boxes indicate major points of use. The grey ovals indicate major P sinks. Point "A" denotes the flow of P contained in treated or untreated sewage to natural water bodies and represents approximately 1.5 Mt P/year. Point "B" denotes the flow of P contained in erosion losses and is about 8 Mt P/year. *Other uses includes industrial uses such as the production of some detergents.

With increasing global populations and increased difficulty in accessing P reserves, many studies have raised concerns regarding depletion of mined P sources (Childers et al., 2011; Cordell et al., 2011, 2009; Cordell and Neset, 2014; Gilbert, 2009; Smil, 2000; Withers et al., 2014). Mined P rock exists mostly in ancient marine sedimentary deposits, the majority of

which are situated in Morocco and Western Sahara (Van Kauwenbergh et al., 2013). Estimated at ca 67 000 Mt (USGS, 2014), the global production of P rock is widely thought to hit a peak this century (Walan et al., 2014), with some predicting that economically mineable P rock reserves could become scarce or exhausted within 100 years (Childers et al., 2011; Cooper et al., 2011; Smil, 2000). The decreasing quality of P rock, in terms of contamination with cadmium for example (Mar and Okazaki, 2012), and price spike events (Mew, 2016) are additional concerns. With an expanding global population relying on decreasing and deteriorating P resources, the development of technologies for improved recovery and re-use of P is becoming an increasingly urgent environmental, economic and societal issue. The rising cost of P rock extraction will inevitably favour the development of these technologies.

WWTPs provide one of the biggest opportunities for P recovery (Schoumans et al., 2015; Smil, 2000) given the relatively high and constant P load in sewage. The recovery of P from wastewaters can provide an array of benefits: (1) meeting the effluent P limits required by legislation; (2) reducing eutrophication problems; and (3) providing a potential source of fertiliser of agricultural and economic value. The latter simultaneously reduces the reliance on inorganic (rock-P derived) fertilisers in agriculture.

However, municipal wastewaters contain many contaminants, both organic and inorganic, including heavy metals and metalloids (Nguyen et al., 2013), pesticides (Köck-Schulmeyer et al., 2013), pharmaceuticals (Antoniou et al., 2013), personal care products (Brausch and Rand, 2011), nanomaterials, perfluorinated compounds (PFCs) (Richardson and Ternes, 2014), hormones (Loos et al., 2013), recreational drugs (Wilkinson et al., 2016) and pathogens (Cai and Zhang, 2013). Therefore, the application of untreated effluent to agricultural land would pose associated risks to human food consumption (Schoumans et al.,

2015). Hence, wastewaters generally require recovery processes with a certain degree of selectivity to remove P into a solid form that can be safely and effectively used as fertiliser.

Here we critically review P recovery technologies currently used in WWTP processes (chemical precipitation, enhanced biological P removal (EBPR), various sludge treatments, struvite and Ca-P crystallisation, and thermochemical treatment) and other emerging technological options, particularly with respect to recovery efficiency and the use of recovered P as a mineral-P substitute. We conclude this review by providing some recommendations for future work, namely the diversification of technological approaches to recover P and further consideration of the bioavailability and potential contamination of recovered products.

2 Management of P within WWTPs

2.1 Capture and accumulation of P – an overview

P exists in a variety of forms within wastewater and these vary throughout the WWTP process; P in particulate forms are more easily and completely removed through clarification steps (Dueñas et al., 2003) whereas dissolved P species, both organic and inorganic, require more targeted chemical or biological processes for their removal. P concentrations reported for municipal wastewaters are generally below 10 mg P/L (Kim and Chung, 2014; Petzet and Cornel, 2013; Qiu and Ting, 2014; Yuan et al., 2012).

Preliminary screening is firstly applied in WWTPs to remove larger particles followed by a primary treatment step. This involves the settlement and removal of suspended solids and organic fractions, which can be achieved by chemical addition or filtration (Tchobanoglous et al., 2014). Petzet and Cornel (2013) report that 17–26% of an incoming total P load, predominantly in particulate forms, can be transferred to primary sludge in initial settlement

at a WWTP. Secondary treatment, especially in larger WWTPs and those discharging to sensitive environments, is then applied (European Commission, 1991). This can involve the use of microbes to break down soluble organic compounds that remain after the preliminary and primary treatment steps (through trickling filter beds or other treatments), and/or the addition of chemicals to promote the coagulation and flocculation of solids. Other than particulate P removed here through secondary clarification, specific P removal techniques such as chemical precipitation or enhanced biological phosphorus removal (EBPR) can be integrated into the treatment process to target dissolved forms of P. Tertiary and advanced treatments are applied for the further removal or degradation of dissolved contaminants, especially when the treated water will be reused. Aside from addressing ecological and statutory issues, P removal at WWTPs prevents the build-up and blockage of pipes by crystalline deposits and precipitates of P (De-Bashan and Bashan, 2004; Rittmann et al., 2011).

Standard primary and secondary treatments often do not remove sufficient P to meet the required discharge concentration. Under normal secondary treatment (the activated sludge process) around 31–48% of influent P can be transferred into sludge (Petzet and Cornel, 2013). With the P removed through primary settlement, this can leave up to approximately 50% of the total influent P load to be removed by an enhanced P removal technique before discharge into a receiving water body (Desmidt et al., 2015).

Techniques specifically used to remove P from wastewaters can be operationally categorised as chemical, biological or physical. They include the established techniques of chemical precipitation and enhanced biological phosphorus removal (EBPR). In each case P is removed by the conversion of the various dissolved P forms into a solid (De-Bashan and Bashan, 2004).

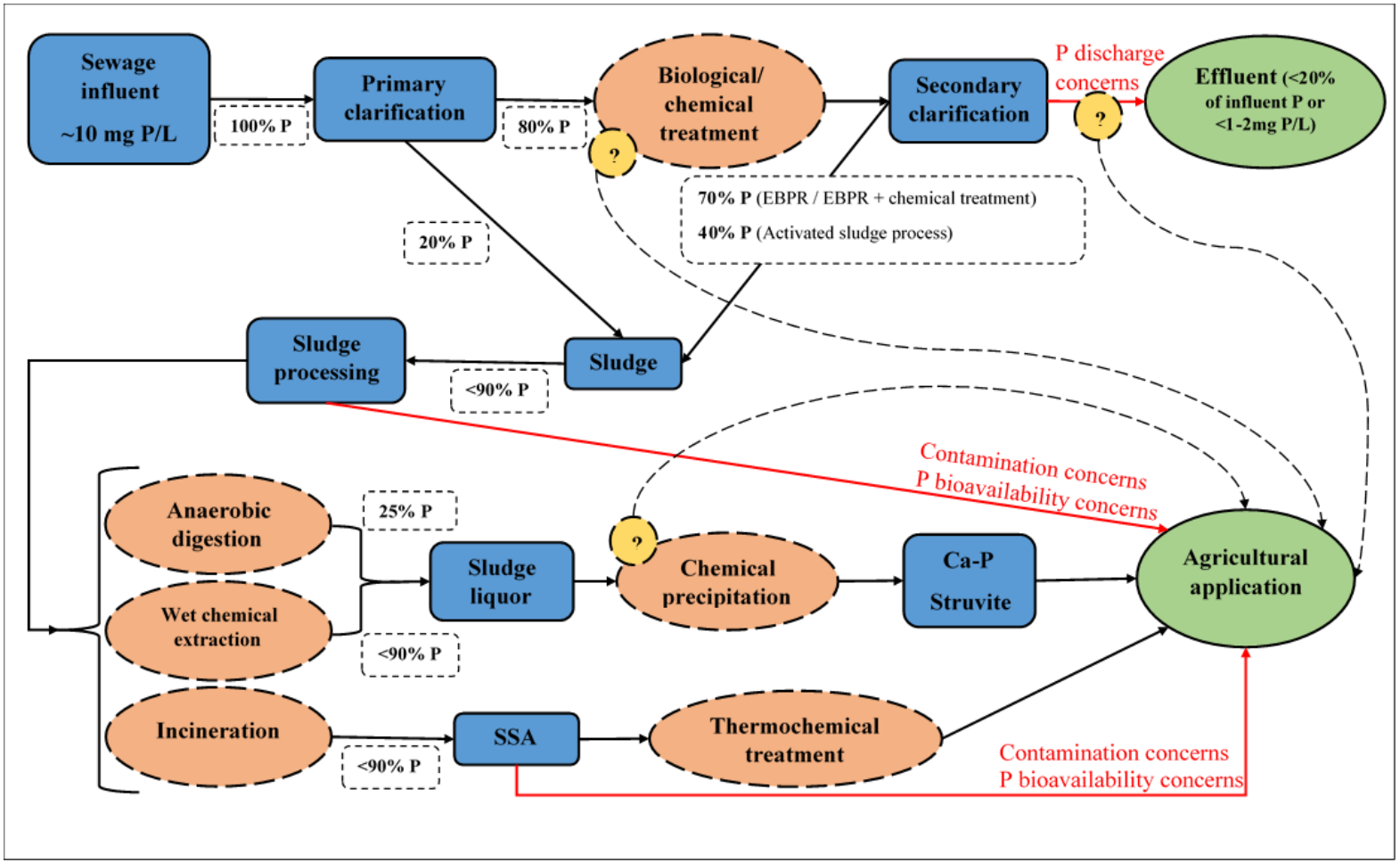

Figure 2. The flow of P through a typical WWTP process, the positions of P recovery technologies (dashed circles) and routes of application of recovered P to agriculture with concerns highlighted in red. Percentage of P (white boxes with dashed line) represents what can be approximately assumed to be removed or carried over to the next treatment stage as a percentage of the influent P load. The dashed yellow circles with question marks indicate where emerging technological approaches could target P recovery.

2.2 Chemical precipitation

Precipitation was first attempted to control eutrophication problems in the 1950s (Morse et al., 1998) and is the main commercial approach to P removal today (Wendling et al., 2013). The precipitative removal of P is usually achieved through the addition of di- or trivalent metal salts of Fe, Al or Ca (Table 1). P in the form HPO_4^{2-}, $H_2PO_4^-$ or H_3PO_4 (dependent upon reaction pH), as well as organic P and particulate P fractions, are coagulated to form a metal phosphate sludge and subsequently removed after flocculation and settlement. Chemical precipitation is more efficient at earlier stages in the waste water treatment process when the concentration of P in solution is highest. Processes involving seeded precipitation, where crystallisation is encouraged and controlled through the addition of a seed material, are being developed to offer more efficient and less costly treatment (Petzet et al., 2012; Song et al., 2006).

Fe and Al salts are considered the most suitable and are generally added as chlorides or sulphates (Morse et al., 1998), calcium can also be used and is generally added as lime ($Ca(OH)_2$). Fe salts are generally preferred as they are cheaper than Al – Fe-P chemistry relating the municipal wastewater is discussed in detail elsewhere (Wilfert et al., 2015).

In terms of emerging options, a recent study has investigated the use of potassium ferrate for P precipitation combined with water disinfection (Kwon et al., 2013). The latter arises from its status as a powerful oxidant while precipitation and coagulation of Fe-P occurs through reduction of Fe (VI). The disinfection rate obtained was faster than for chlorine of the same concentration. Within secondary effluent (1.46 mg total P/L), ferrate was able to remove more than 80% of P in the dosage range of 5–25 mg Fe/L. The two most obvious disadvantages of chemical precipitation are the requirement and cost of chemical additions,

and the generation of large volumes of sludge that are often unsuitable for reuse due to the low recoverability of P and possible incorporation of contaminants in the P-rich precipitate.

Table 1. Details of the three metals conventionally used in the chemical precipitation of P in WWTPs, including the optimal pH for the process, the most common precipitates formed and the advantages and disadvantages of using each.

Element	Optimal pH	Most common precipitate form	Advantages	Disadvantages
Fe	4.5–5 (Thistleton et al., 2002)	Strengite ($FePO_4 \cdot 2H_2O$) (Grzmil and Wronkowski, 2006)	• Relatively inexpensive • Effective in the precipitation of P	• Precipitate unsuitable for use as fertiliser.
Al	~6 (Lin and Carlson, 1975)	Variscite ($AlPO_4 \cdot 2H_2O$) (Lin and Carlson, 1975)	• Most effective precipitant. (Yeoman et al., 1988) • At pH 6, both biological treatment and precipitation with Al could be operated.	• Expensive • Precipitate unsuitable for use as fertiliser • Doses of >60mg Al/L have a toxic effect on autotrophic bacteria within a membrane bioreactor (Zahid and El-Shafai, 2012) – dosage must be carefully considered.
Ca	>10.5 (Jenkins et al., 1971)	Hydroxyapatite ($Ca_5(PO_4)_3OH$)	• Relatively inexpensive • Ca-P precipitates can be similar in form to rock-P and suitable for use in industry • Potentially suitable as fertiliser	• High pH requirement • High pH can create detrimental conditions for biological treatment • Additional neutralisation step may be required • Large volume of generated sludge

Numerous by-products and wastes have also been investigated as potential precipitants. Red mud, an abundant mining waste, has been studied for its potential for precipitation of P due to its high content of Al and Fe. Through the treatment of red mud, Poulin *et al.* derived a solid product that had P removal efficiency similar to commercial coagulants, namely 70–98% in solutions containing 5–100 mg P/L respectively (Poulin et al., 2008). Municipal solid waste fly ash has also been investigated, with reported removal rates of approximately 6 mg P/g (Zhong et al., 2014). Hydrated oil shale ashes in subsurface flow filters have been assessed in long period pilot-scale experiments treating municipal and landfill leachate wastewater in Estonia, achieving 99% removal from wastewaters ranging in P concentration from 0.13–17.0 mg total P/ L (Kõiv et al., 2010). In this case the direct precipitation of Ca-P was suggested to be the controlling P removal mechanism.

Other waste materials providing strong precipitation effects include calcined waste paper sludge. The formation of brushite ($CaHPO_4 \cdot 2H_2O$) was found to be the main mechanism controlling P removal in a laboratory scale study, which reached 1.5 mmol P/g (46.6 mg P/g) calcined paper sludge (Wajima and Rakovan, 2013). Drinking waterworks sludge was also found to be effective for P removal in laboratory scale experiments due to its high content of Al and Fe: 99% removal could be achieved from an initial concentration of 2 mg P/L and a sludge dose of 10 g/L in synthetic wastewater, at pH value 5–6 (Yang et al., 2014).

2.3 Enhanced biological phosphorus removal (EBPR)

EBPR was developed during the 1970s (Barnard, 1975; Yuan et al., 2012), and is extensively used today. Most full-scale P recovery technologies currently applied require the pre-accumulation of P (as bio-P sludge) using EBPR processes. EBPR relies on polyphosphate accumulating organisms (PAOs) or denitrifying PAOs to accumulate P intracellularly as polyphosphate granules, thus avoiding any requirement for chemical precipitants (Oehmen et

al., 2007; Wong et al., 2013). The process is enabled by alternating anaerobic and aerobic conditions; PAOs take up volatile fatty acids under the anaerobic phase, which are stored as polyhydroxyalkanoates and subsequently metabolised in the aerobic phase to supply the energy needed by the PAO to accumulate P (Kristiansen et al., 2012). Sludge, highly enriched in PAOs, can accumulate as much as 20% cell dry weight as P, compared with 1–2% in non PAO-enriched sludge (Tchobanoglous et al., 2014). Bacterial genus *Acinetobacter* was at first thought to be the primary PAO (Fuhs and Chen, 1975) in EBPR, however members of Actinobacterial genus *Tetrasphaera* (Kong et al., 2005) and the bacteria *Candidatus Accumulibacter Phosphatis* (He and McMahon, 2011; Hesselmann et al., 1999) are now considered to be more responsible for P accumulation in WWTPs (Kristiansen et al., 2012). In addition to bacterial strains, microalgae have been investigated as suitable PAOs for P assimilation in wastewater treatment (Solovchenko et al., 2016).

The accumulation of P within bio-P sludge and its settlement can facilitate the recovery of P and allow for direct utilisation as fertiliser, depending on contaminants present. Alternatively, further treatment can facilitate the solubilisation and recovery of P in a form such as struvite ($MgNH_4PO_4 \cdot 6H_2O$) (Baur, 2009). A recent paper investigated the use of microalgae and cyanobacterial strains for the accumulation of P from parboiled rice mill effluent. These P enriched PAOs showed moderate P release as a biofertiliser and was comparable to that of commercial fertilisers (Mukherjee et al., 2015).

In full scale WWTPs, EBPR processes can typically remove over 85% of P in municipal wastewater influent, often to concentrations <0.1mg P/L (Gautam et al., 2014; Gebremariam et al., 2011). Although efficient in many cases, there are however questions over the stability of its performance (Oehmen et al., 2007; Zheng et al., 2014). Various process inefficiencies and failures are reported to be associated with EBPR. One of the largest causes of deterioration and failure in EBPR systems arises from the occurrence of glycogen

accumulating organisms (GAOs) (López-Vázquez et al., 2008), which compete with PAOs for carbon substrate (Oehmen et al., 2007; Yuan et al., 2012). GAOs can function under aerobic or anaerobic conditions (Zheng et al., 2014) and are found widely in EBPR processes (Burow et al., 2007). Considerable effort has therefore been focused on establishing the conditions that might limit their growth (Oehmen et al., 2006, 2005, 2004; Wang et al., 2010; Whang and Park, 2006, 2002; Whang et al., 2007). This has established that at pH 8, the abundance of GAOs is restricted while optimal PAO activity is maintained (Oehmen et al., 2005). The type of carbon substrate and its concentration is also important (Shen and Zhou, 2016); propionate for example was found to be more beneficial than acetate for PAO growth (Wang et al., 2010; Zeng et al., 2013). The presence of toxic substances in the influent, such as Cr (VI) (≥0.5 mg/L), can also inhibit P removal, being toxic to PAOs (J. Fang et al., 2015).

Without carbon addition to ensure high and constant concentrations, the EBPR system can be very susceptible to changes in the influent composition. Consequently, climates with a tendency for sporadic heavy rainfall, which can drastically perturb nutrient concentrations, can affect biological P removal (Manyumba et al., 2009). The addition of organic carbon to the process however is unfavourable as it incurs additional cost to the EBPR process and increases the overall carbon footprint (Guerrero et al., 2015). Organic carbon additions derived from waste sources have been successfully investigated which may reduce cost and increase the sustainability of the process; waste activated sludge fermentation liquid was found to be a more effective carbon source that acetic acid (Ji and Chen, 2010), crude glycerol, a biodiesel waste product, was successfully dosed in an EBPR process and resulted in better control over P removal (Guerrero et al., 2015).

High temperatures, 30°C as opposed to 20°C, encourage GAO growth (Whang and Park, 2002) with lower temperatures found to be beneficial for PAO growth (López-Vázquez et al., 2008) and therefore P removal. Low aeration rates and thus low dissolved oxygen (DO) also

favour PAOs over GAOs (Carvalheira et al., 2014). These variables may impact on the final P concentrations in the treated effluents and discharges may exceed those permitted by legislation.

EBPR processes are considered to be a more sustainable compared to chemical processes and can often offer significant economic advantages in larger WWTPs (Manyumba et al., 2009). EBPR requires less or no chemical addition and has the potential for the full-scale recovery of P. However, where process inefficiencies are frequent and/or legislation requires consistently low P concentrations in effluent discharge, it is also common for larger WWTPs to deploy chemical precipitation in conjunction with EBPR to ensure requirements are consistently met (Kim and Chung, 2014; Kwon et al., 2013). This reduces the amount of P that can be solubilised and recovered through bio-P sludge digestion or direct application as fertiliser. Other limitations include the complexity of operations and a large energy and space requirement (Nguyen et al., 2014a). The future use of EBPR processes may therefore not extend beyond those WWTPs with a relatively narrow geographic, spatial and economic context.

3 Sludge enhancement and P recovery from sludge

A major disadvantage of chemical precipitation of P is the possible co-precipitation of toxic ions such as arsenic and fluoride as well as organic contaminants, pathogens or viruses (Mehta et al., 2014) among others. This is highly relevant in terms of the handling of the final product and its suitability for land application. The potential for precipitation using Al and Fe to yield suitable P-bearing soil amendments is limited, since Al can be toxic to many plants at high concentration, especially in acidic soils (Poschenrieder et al., 2008), and P in Al- and Fe-P solids may limit the P solubility to plants and is considered unrecoverable for the purpose of fertiliser production (Donnert and Salecker, 1999; Wendling et al., 2013).

The direct application of dewatered bio-P sludge has been found to be as effective as mineral fertiliser (Erdincler and Seyhan, 2006; Kahiluoto et al., 2015), but similarly, there are increasing concerns over the transfer of chemical and biological contaminants to the environment, affecting food supply (De-Bashan and Bashan, 2004; Krzyzanowski et al., 2014; Yuan et al., 2012). It has been shown that sewage sludge application to soil, although it increases the available nutrient content of the soil, also increases heavy metal concentration in both soil and plant. At a sludge application dose of 20 t/ha or higher, Cd concentrations in rice grain were found to be above the Indian safe limit (Latare et al., 2014). Switzerland has already banned the use of sewage sludge in agriculture (Franz, 2008; Schoumans et al., 2015).

Other issues with the direct application of sewage sludge include the difficulty in its transportation and application, given that sludges are bulky and dense. Dewatering of sludge can reduce haulage costs and removes the necessity for specialist farm equipment, but incurs energy and financial costs (Yuan et al., 2012). The recovery of P from WWTP sludges in purer and more effective forms than that derived directly from sewage sludge is being sought through the approaches outlined in the following subsections, which includes a number of emergent technologies. These approaches are becoming necessary to ensure the safe recovery of P and compliance with current and future legislation.

3.1 Anaerobic digestion and dewatering

Anaerobic digestion (AD) is the process most commonly used for stabilisation of sludge, offering organic solids and pathogen destruction as well as energy recovery in the form of methane (Mehta et al., 2014; Tchobanoglous et al., 2014). AD of bio-P sludges can generate a liquor of approximately 10–50 times higher P concentration than the WWTP influent (Yuan et al., 2012). The majority of the heavy metal load is retained within the sludge, whilst P is

released from the biodegradable fractions into the liquid phase. In terms of emerging organic contaminants, it was shown that within AD processes, detected emerging contaminants such as the antidepressant venlafaxine and benzoylecgonine, the main metabolite of cocaine, were preferentially adsorbed and concentrated within the solid material; the majority of the 13 compounds detected were not degraded by AD processes (Boix et al., 2016).

Concentrations of P in the supernatant of AD processes can vary considerably: 30% of total P has been estimated to be dissolved in the aqueous phase arising from AD of bio-P sludge, whereas <10% is thought to be dissolved after AD of chemical sludges (Petzet and Cornel, 2013). This is due to the re-fixation of P into the sludge through precipitation with Fe, Al, Ca and Mg or through adsorption (Petzet and Cornel, 2012). AD of bio-P sludge as a solubilisation technique is a primary step in facilitating the precipitation of struvite in many commercial P recovery processes such as Crystalactor®, NuReSys®, Pearl®, Phosnix® and PHOSPAQ™ (Schoumans et al., 2015). Assimilation of solubilised compounds, in particular emerging organic contaminants, found in AD supernatants into final recovered P products such as struvite may be of particular concern and warrants further investigation.

3.2 Wet chemical extraction

Wet chemical extraction, involving either acid or alkaline dissolution, supports greater solubilisation of P from sludge, sludge ash or other sludge residues, although it can simultaneously solubilise contaminants, of which heavy metals/metalloids are of particular concern. Therefore, the separation of metals and P is highly important when operating wet chemical extraction for P recovery. Additionally, because in recovery through struvite crystallisation, Fe, Al and Ca can compete with Mg to form complexes with orthophosphate, their minimisation leads to improving the efficiency of the recovery process.

Through the acid digestion of various forms of digested sludge, using sulphuric acid (pH 1.8), it has been established that incineration – compared to original, diluted and centrifuged digested sludges – is the better preliminary step for precipitation of struvite. This is because Al, Ca, and Fe could be removed to the greatest extent (98%, 97%, and 80% respectively) (Güney et al., 2008). However, for the effectiveness of P solubilisation, Fe-PO_4-containing raw sewage sludge was more beneficial for the release of P (Sano et al., 2012). Advantages to using alkali extraction as opposed to acid extraction, is that the release of heavy metals/metalloids can be suppressed to lower levels. This may limit the need for filtration technologies, which can be costly and prone to fouling. However, alkali treatment can also reduce the recovery of P to as low as 30% (Mattenberger et al., 2008).

The PHOXNAN (Blöcher et al., 2012) process involves the release and accumulation of P from sludge into a solution suitable for recovery through wet oxidation by the addition of sulphuric acid (pH 1.5). P resides in the resulting solution as H_3PO_4, while the organic content is decreased and other micro-organic pollutants are oxidised. An ultrafiltration membrane separates the remaining solids, a step that is followed by nanofiltration to remove cations. P is accumulated in the final solution mainly as phosphoric acid. In another study, alkaline hydrolysis of excess secondary sludge from an anaerobic/aerobic process was carried out at an optimal pH value of 13, with both P and N being recoverable from the supernatant (Bi et al., 2014). The process enables the release and recovery of 42.0 % PO_4^{3-} (P) and 7.8 % NH_4^+ (N) in the form of struvite. The treatment of sludge with supercritical water gasification was found to release up to 95.5 % P (Acelas et al., 2014). In this case, oxalic acid was reported to have a better performance than sulphuric acid in the leaching of P.

Neither acid nor alkali treatments offer an ideal option for the full solubilisation and recovery of P. The choice of treatment should be considered carefully with respect to the initial accumulation of P in primary and/or secondary treatment. Petzet *et al.* reported that P

recovery via wet chemical treatment of sewage sludge ash (SSA) could be optimised by a combination of both acid and alkaline leaching (Petzet et al., 2012). Through an acidic pre-treatment, alkaline insoluble Ca-P fractions are converted to Al-P which can then be easily dissolved through alkaline treatment and separated through the precipitation of Ca-P. The Al fraction can then be reused in chemical precipitation processes in the primary stream. For WWTPs using Al based precipitation and thus generating a high Al SSA, the P-recovery rates were found to be as high as 70–77%. Even where Fe-based precipitation was operated, it was reported that a considerable amount of the required Al is supplied by the decay products of detergent zeolites (Petzet et al., 2012).

3.3 Incineration and P release from sewage sludge ash

The incineration of sludge provides complete oxidation of organic constituents at high temperatures. Mono-incineration, where the sludge is incinerated separately to other wastes, can be a favoured option since it can greatly decrease sludge volume, energy can be recovered and, since phosphate is thermally stable and does not volatilise during the process, P is retained and concentrated in the ash. SSA has been found to contain on average 11.6% P_2O_5 (Cyr et al., 2007) (a form and content comparable to P-rock ores) (Aydin et al., 2010; Weigand et al., 2013). SSA is not generally appropriate for direct application to land however, due to the retention of heavy metals/metalloids and the strong binding of P (Ottosen et al., 2014) due to higher crystallinity of P_2O_5 generated at higher temperatures. In solubility tests with ammonium citrate, one indicator of short-term bioavailability, only 26% of P present in SSA was found bioavailable (Krüger and Adam, 2015). The recovery of P in a purer form may increase the bioavailability of P and reduce the contamination risk.

The release of P from SSA can be achieved by the dissolution of the ashes in acid, the separation of heavy metals and the precipitation of calcium phosphate, ferric hydroxide and

aluminium hydroxide, as in the Ash2®Phos process. This process is reportedly economically profitable since it is dealing with a waste which would otherwise incur a cost for disposal and the commercial products produced (mono/di-ammonium-phosphate and Fe and Al precipitants) (EasyMining-Sweden, 2017). P content (>95%) from SSA was recovered by acidification with HCl (Xu et al., 2012). Heavy metals were subsequently removed from solution using a cation exchange resin. P was recovered in the form of struvite (97% pure), which has high P bioavailability of 94% and low metal content, thus comparable to a high quality fertiliser. Electrodialysis was also studied as an option for the separation of heavy metals/metalloids and P after pre-treatment with sulphuric acid. The process separated P from heavy metals/metalloids effectively with up to 70% mobilisation of the P from the SSA (Guedes et al., 2014).

421 **Table 2.** Examples of commercial processes for P recovery and the form of the final P product derived.

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Process	Information and process description	Final product	Reference
AirPrex® process	Crystallisation of struvite applied directly in the digested sludge stream. CO_2 is stripped to increase pH. $MgCl_2$ is added. AirPrex® systems are currently operational at several WWTPs in Germany and The Netherlands. The world's largest AirPrex® system is being constructed at the WWTP of Amsterdam. Developed by Berliner Wasserbetriebe (Germany).	Struvite	(Eliquo Water & Energy BV, 2016; Tchobanoglous et al., 2014)
DHV Crystalactor®	The sludge side stream is fed into the reactor and recirculated. Quartz sand is initially added as seed material to accelerate precipitation. Pellets settle to the bottom. Developed by DHV (NL).	Struvite, Mg-P or Ca-P	(Giesen, 2016; Tchobanoglous et al., 2014)
NuReSys® process	Air is initially added and CO_2 is stripped from the side stream followed by $MgCl_2$ addition in the stirred crystalliser tank where struvite forms pellets. NaOH is added to maintain pH in the range 8.1-8.3. Pellet size can be controlled by stirring speed. Developed by Akwadok/NuReSys (Belgium).	Struvite	(NuReSys, 2016; Tchobanoglous et al., 2014)
Ostara Pearl® process	Struvite crystallisation is achieved through treatment of sludge side stream in a fluidised bed crystalliser. Effluent is recirculated and $MgCl_2$ and NaOH are added as the Mg source and for pH maintenance respectively. Developed at the University of British Columbia and introduced at full-scale by Ostara Nutrients Recovery Technologies Inc. (USA).	Struvite (Crystal Green®)	(Ostara, 2016; Tchobanoglous et al., 2014)
Phosnix® process	A cylindrical reaction zone with a conical bottom section is applied. $Mg(OH)_2$ and NaOH added as a source of Mg and for the control of pH respectively, and aerated to strip CO_2. Struvite settles to the bottom where it is removed with the effluent recirculated. Developed by Unitika Ltd (Japan).	Struvite	(Katsuura, 1998; Tchobanoglous et al., 2014)
PHOSPAQ™ process	A side stream process consisting within an aerated zone. Air lift is designed to provide mixing, strip CO_2 and increase pH, and provide DO for biological treatment. MgO is used as the Mg source for the precipitation of struvite. Developed by Paques (The Netherlands).	Struvite	(PAQUES, 2016; Tchobanoglous et al., 2014)

FIX-Phos	Calcium silicate hydrate (CSH) particles are added into the anaerobic digester. The CSH adsorbs P as Ca-P and controls struvite formation by reducing the P concentration in the digestate. The Ca-P on CSH can be separated and recovered from the digested sludge.	Ca-P on CSH	(Petzet and Cornel, 2012)
P-RoC®	P recovery from waste water similar to the Crystalactor® process however complex pre-treatment steps such as pH adjustment or CO_2 stripping can reportedly be avoided. Crystallisation products showed a P content of 11 % to 13 % which was comparable to phosphate rock.	Ca-P on CSH	(Berg et al., 2001)
PHOXNAN	The process combines low pressure wet oxidation with two membrane filtration steps. High temperature and pressure at acidic conditions (sulphuric acid added to adjust pH to 1.5) are used for sludge oxidation with pure oxygen. Organic components are decreased and organic pollutants are oxidised. Due to the low pH, P exists in solution mainly as H_3PO_4 and H_2PO_4. The first membrane uses ultrafiltration to separate solids, the second membrane uses nanofiltration to eliminate metal ions.	H_3PO_4	(Blöcher et al., 2012)
Aqua Reci	Commercially, the process makes use of supercritical water oxidation. Leaching is accomplished with a base, which selectively dissolves P. By addition of calcium, P can be precipitated.	Ca-P	(Levlin, 2007; Stendahl and Jäfverström, 2004)
EcoPhos®	HCl or H_2SO_4 is used for the digestion of any phosphate raw material including P-rock or SSA. The EcoPhos® process involves the treatment of the obtained slurry to remove dissolved impurities and solid residues and produces a phosphate product such as dicalcium phosphate or H_3PO_4.	DCP or H_3PO_4	(DeRuiter, 2014; Ecophos, 2017)
Mephrec	The process utilises temperatures of up to 2000 °C where the sewage sludge melts under the addition of oxygen, with all organic pollutants destroyed. The metals obtained can be recycled, the slag is a form of fertilizer with high plant availability, free of heavy metals/metalloids and organic pollutants – similar to Thomas phosphate fertiliser (a P-rich slag produced in the steel industry).	Detoxified mineral P	(Nuremberg GmbH, 2016)
AshDec	Ash and natural earth alkali salts are exposed to a temperature of 1 000-1050°C. The heavy metals/metalloids react with the salts, become gaseous and evaporate. The phosphate compounds are transformed into plant available species.	Detoxified mineral P	(Outotec, 2017)

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4 Recovered P products from treated sludge

P recovery processes from sewage sludge, including commercial and large scale approaches and the characteristics of the final products obtained are detailed in Table 2. Recent description and comparison of commercial approaches for P recovery from municipal wastewater is provided in detail elsewhere (Egle et al., 2016, 2015). Current EU fertiliser regulation recognises only primary mineral-derived P products as fertiliser whereas the rest of these recovered P products cannot yet be labelled as such (European Union, 2003) – the legislation however is currently under revision to include recovered P residues such as struvite, ashes and pyrolysis materials (European Commission, 2016; Huygens et al., 2017). This revision also limits the composition of fertiliser products in terms of impurities and level and bioavailability of nutrients, therefore selective routes to obtain these products will be beneficial. Among the recovered products in Table 2, struvite stands out due to its usability directly as a slow release fertiliser (Bouropoulos and Koutsoukos, 2000).

4.1 Struvite

Struvite precipitation has been the main focus for P recovery commercially, and is widely recommended for treatment of sludge digester liquors in large WWTPs operating EBPR processes (Martí et al., 2010). Struvite crystallises as hard crystalline deposits when a molar ratio and concentration of $Mg:NH_4:PO_4$ exists of 1:1:1 and exceeds the product solubility constant, respectively (Crutchik and Garrido, 2016). For crystallisation to occur readily, a concentration between 100 and 200 mg PO_4^{3-}/L is required (Rittmann et al., 2011), which tends to be at least 10 times higher than typically found in the liquid phases of municipal wastewater treatment. The crystallisation of struvite and other P-rich precipitates results in a very low degree of impurities. This is advantageous because the selectivity of this process

leads to a safe product that can be applied to soil directly, despite the possible presence of heavy metals and other contaminants in the EPBR effluents. Solution pH can be increased by the addition of a base or through CO_2 stripping (Petzet and Cornel, 2013); struvite becomes highly insoluble at alkaline pH and therefore increasing solution pH can lead to increased and accelerated struvite formation (Ariyanto et al., 2014). The effective precipitation of struvite has been shown feasible in the treatment of side streams originating from the digestion of EBPR sludge (Mattenberger et al., 2008). Practically and economically, however, struvite production is currently viable only in large WWTPs where enhanced biological accumulation of P can be applied.

The precipitation of struvite is usually initiated with the addition of a Mg source as most municipal wastewaters contain more N and P than Mg (Rahman et al., 2014), however some streams can require PO_4^{3-} additions where the P content is low. The source of Mg used may contribute up to 75% of the overall production costs of struvite (Dockhorn, 2009), however if P is accumulated using EBPR then Mg may be the only chemical requirement in the WWTP process. The most common source of additional Mg is $MgCl_2$ or MgO, though many other materials have been used experimentally. Lahav *et al.* (2013) investigated using concentrate from seawater nanofiltration as a cheap Mg (II) source for precipitating struvite from municipal sludge centrifuge wastewater. Wood ash and bittern salts have also been found to be good sources of Mg in struvite crystallisation processes (Lee et al., 2003; Sakthivel et al., 2012).

Where chemical precipitation is operated, Fe or Al may be present at high concentrations. P may consequently co-precipitate during solubilisation in AD or other WWTP processes. A stream of sufficiently concentrated P may then not be available to support effective struvite precipitation and ensure high rates of P recovery. High Ca^{2+}/PO_4^{3-} ratios have been found to

be detrimental to struvite formation in pilot- and full-scale plants treating potato and dairy wastewater, respectively (Moerman et al., 2009).

Uncontrolled precipitation of struvite can occur within centrifuges, digesters and sludge liquor pipes (Petzet and Cornel, 2012). Where the controlled precipitation of struvite is carried out in side stream processes, after the dewatering of the digested sludge, this undesired precipitation can make the processes less efficient with potential additional costs being incurred from the maintenance of equipment. The commercial Airprex® process (Table 2) precipitates struvite directly in the sludge stream and can therefore have economic benefits regarding scaling of pipes and sludge dewatering equipment. The recovery of the struvite then depends on the subsequent separation of digested sludge. Waternet, Amsterdam, which recovers P as struvite from bio-P sludge using the Airprex® process, reportedly makes an annual saving of €500 000 due to improved dewatering and reduced scaling problems – the recovered struvite product is sold to the fertiliser industry for between €50–100/t for fertiliser production (Waternet, 2017). For the use of struvite in agriculture it is important to minimise contaminants, for example heavy metals and metalloids may become incorporated into the precipitated struvite. Arsenic, for example, has been found sequestered into a synthetic struvite at concentrations of up to 547±15 mg/kg (Lin et al., 2013). This potentially renders struvite recovered from some waste streams unusable in agriculture without removal of heavy metals/metalloids.

Struvite has an economic value as an effective slow release fertiliser, for example it was sold in Japan at a USD value of $250 per tonne in 2001 (Forrest et al., 2008; Ueno and Fujii, 2001). Other than in municipal WWTPs, struvite precipitation has recently been investigated in a broad variety of wastewater streams from bakery production (Uysal et al., 2014); the semiconductor industry (Warmadewanthi and Liu, 2009); swine and poultry farming (Jordaan et al., 2010; Taddeo and Lepisto, 2015; Yang et al., 2012); slaughterhouse wastewater

(Kabdaşli et al., 2009); landfill leachate (Huang et al., 2014); human urine (Lind et al., 2000) and within the potato processing industry (Uysal and Kuru, 2013). Some studies have been found effective, in precipitating struvite from agro-industrial wastewaters, at pilot- and full-scale (Moerman et al., 2009), whereas largely, studies still remain to be proven effective at full-scales.

4.2 Ca-P precipitates

P content in recovered Ca-P products can vary from 12–20% and can be assumed to have a higher solubility than that of well-crystallised Ca-P (Cabeza et al., 2011). From a commercial viewpoint, however, the recovery of P in the form of Ca-P is beneficial since it has more diverse applications in industry than struvite (Okano et al., 2013). Calcium phosphate (mainly as hydroxyapatite, $Ca_5(PO_4)_3OH$) reflects the composition of rock phosphate and should be easily adopted as a secondary P source in existing industry and infrastructure (Song et al., 2006; Tervahauta et al., 2014). Indeed, many established commercial processes already derive Ca-P precipitates as the final product (Table 2).

Hydroxyapatite is the most common form of Ca-P precipitate and forms at high pH, typically >10 (Rittmann et al., 2011). At lower pH, dicalcium phosphate dihydrate ($CaHPO_4\,2H_2O$) and octacalcium phosphate ($Ca_8H_2(PO_4)_6\,.5H_2O$) are expected to be the more stable phases. However, these precipitated phases are thought to transform into the more thermodynamically stable hydroxyapatite over time (Desmidt et al., 2015; Seckler et al., 1996).

Calcium silicate hydrates (CSHs) have been studied as a seed for Ca-P precipitates. Amorphous CSHs (Okano et al., 2013) and tobermorite-rich waste materials from the construction industry (P-RoC) (Berg et al., 2001) have been investigated. Other calcium rich materials investigated include cattle bone (Jang and Kang, 2002). In the precipitation of Ca-P,

bicarbonate alkalinity often requires control as competition between hydroxyapatite and calcium carbonate precipitation can occur. This is often provided through the removal of carbonates by acidification and CO_2 stripping, but the addition of a base such as NaOH to increase pH can increase the cost of the process. It has been noted, however, that using CSH as a seed material avoids the need to modify the influent and that removal of carbonate was unnecessary, with phosphate and carbonate co-precipitated to the solid surface (Song et al., 2006).

Commercial processes based on Ca-P precipitation include *FIX-Phos,* in which Ca-P is directly precipitated (on CSH) into sludge. This holds the same risks identified for the corresponding struvite process (see section 4.1).

4.3 Thermochemically treated sewage sludge ash

Thermochemical treatment is an option for deriving a metal-depleted solid with higher bioavailable P. After mono-incineration, the addition of Mg and Ca chlorinated salts and water, thermochemical treatment at approximately 1000°C was found to increase P-bioavailability due to the formation of Mg- and Ca- bearing phosphates such as chlorapatite, farringtonite and stanfieldite (Adam et al., 2009). Heavy metals/metalloids are depleted mainly due to their volatilisation as heavy metal chlorides. The legal limits of Fertilizer Ordinance in the EU were reportedly met in most cases. KCl added to SSA favoured Cu removal over Zn, but the converse was the case for $MgCl_2$ (Mattenberger et al., 2008). This has relevance to the thermochemical treatment of incinerated biological sludges since they tend to contain higher concentrations of Cu and Zn (Franz, 2008). In most cases Cd, Cu, Zn and Pb can be removed up to at least 90 wt% from SSA. However, even with higher Cl addition at the same incineration temperatures (1000°C), Cr and Ni have been found to have low volatility (Fraissler et al., 2009; Vogel and Adam, 2011).

Two commercial processes in the literature, AshDec and Mephrec, offer recovered products in the form of mineral-P from thermochemical SSA treatment. The AshDec process is a calcination process based on fluidised bed technology (Outotec, 2017). The Mephrec process, through metallurgic treatment at high temperature, provides a slag that contains P of high plant availability, free from heavy metals/metalloids and organic pollutants, and similar in form to Thomas-phosphate fertiliser. This is used by the fertiliser industry after further processing but can be safely used in organic farming (Nuremberg GmbH, 2016).

5 Experimental P recovery through sorption processes

Several experimental technologies are being developed that have shown high efficiency for P recovery at bench or small pilot scale: membrane filtration (Gerardo et al., 2015; Qiu and Ting, 2014), electrodialysis (Zhang et al., 2013), and nanoparticle-based sorbents (Lu et al., 2015; Su et al., 2015; Tu and You, 2014) as well as various modified mineral- and biological-based sorbents (Chiou et al., 2015; C. Fang et al., 2015; Nguyen et al., 2014b; Yu et al., 2015). However, cost and practicality have so far prevented these technologies from being adopted in commercial scale operations.

Sorption techniques have been shown to have potential for removal of a wide range of contaminants from dilute wastewater effluents (Busquets et al., 2014; Nguyen et al., 2013; Sivasankar et al., 2013). The use of easily obtainable or synthesisable materials as well as waste materials may reduce the need for more expensive chemical additives or modification to existing WWTP infrastructures. As well as encouraging the precipitation of P by seeding, mentioned in preceding sections, sorbent-based processes can include other coexisting mechanisms such as ion exchange, ligand exchange, and electrostatic interactions to directly sorb P from the waste stream. Such processes can potentially fit into existing WWTP infrastructures and provide enhanced P removal and recovery. Sorbents have not been widely

employed in WWTPs as stand-alone P recovery processes. Similarly, the potential of recovered sorbed-P fertiliser or soil amendment has not been widely considered or assessed. However, a wide variety of materials evaluated for the sorption of P have shown high potential, these have been compiled in Table 3.

An extensive review of agricultural by-products and wastes for the sorptive removal and recovery of P recently concluded that organic materials require some form of pre-treatment before use in P recovery, due to the lack of anion binding sites (Nguyen et al., 2014a). Surface modifications can significantly enhance the capture efficiency, but poor reusability of materials recycled from agriculture has been reported. Capture and recovery of P by biochars has been investigated and modification of the feedstock, mainly through incorporation of Fe or Mg, has been shown to be necessary to enable efficient uptake of P (Shepherd et al., 2016; Yao et al., 2013). Although the application of P-bearing biochar to soil has been suggested, the technology is still in its infancy. While efficient P removal can be brought about through material modifications, the added cost to the process may make their application to soil uneconomic. Among the potential mineral sorbents zeolitised fly ash, layered double hydroxide (LDH) minerals and Li-intercalated gibbsite have exhibited high potential for P sorption from solution (Wendling et al., 2013). Their subsequent direct use as nutrient bearing soil amendments or as P fertiliser has been suggested, but not yet demonstrated.

586 **Table 3.** Sorbent materials used for the uptake of P: Sorption capacities, application and mechanisms.

Sorbent material	Sorption capacity/ efficiency	Information about study/ experiment	Reference
Powdered sulphate-coated zeolite	111.5mg P/g	Three novel composite adsorbents, sulphate- coated zeolite (SCZ), hydrotalcite (SCH) and activated alumina (SCAA). Sulphate coating improved sorption capacity in the case of SCZ and SCAA. Adsorption thought to have occurred fast. Main mechanism: ion-exchange between phosphate and sulphate on the surface of the adsorbents.	(Choi et al., 2012)
Powdered hydrotalcite	26.1 mg P/g		
Sulphate coated activated alumina	49.7 mg P/g		
Lanthanum hydroxide	107.5 mg P/g	Surface area 153.3 m^2/g. Performed well across a wide range of pH values. Main mechanism: ligand exchange.	(Xie et al., 2014)
Cerium-zirconium binary oxide nanoparticles	36.6 mg P/g	Ce/Zr binary oxide nanoparticles were synthesised with different structure, crystal size, surface properties, and phosphate adsorption performance. Main mechanism: inner-sphere complexing mechanisms were thought to dominate, the surface -OH groups playing a major role.	(Su et al., 2015)
Cement based materials	30.0 mg P/g	High Si, Ca, Al and Fe content within cement materials. Main mechanism: precipitation with Ca predominantly.	(Wang et al., 2014)
Zirconium loaded okara	14.4 mg P/g	The phosphate removal was rapid, reaching 95% in 30 min from an initial concentration of 5 mg P/L. Adsorption tested between 10 – 500 mg P/L.	(Nguyen et al., 2014b)
Magnetic Fe-Zr binary oxide	13.7 mg P/g	Incorporation of Fe into Fe-Zr oxide allows for magnetic recovery. Zr oxide was a suitable adsorbent for P. Main mechanism: ion-exchange of Zr species and partly originated from magnetite species of Fe–Zr binary oxide.	(Long et al., 2011)
Scallop shell synthesized ceramic biomaterials	13.6 mg P/g	Scallop shells, montmorillonite and starch (1:1:1) were mixed to a paste. The ceramic samples were dried at 105°C for 24 h in an oven and calcined at 600°C. A surface area of 53.74 m^2/g was reported.	(Chen et al., 2013)

Nano bimetal ferrites (CuFe2O4 – Green synthesis)	13.5 mg P/g	Manufactured from industrial sludge. Fast sorption rate within first 10mins reached equilibrium within 120mins. Magnetic. Large potential for desorption and recovery. Main mechanism: inner-sphere mechanisms.	(Tu and You, 2014)
Amine-functionalized silica magnetite	>~13 mg P/g	A magnetic adsorbent: amine-functionalized silica magnetite. The maximum adsorption was found to occur at pH 3.0.	(Chiou et al., 2015)
Zirconium loaded bifunctional fibers (fibrous ligand exchange adsorbent)	Breakthrough point at ~340BV	Adsorbent slightly preferred phosphate to arsenate. Sorbent reversible and suitable for multiple reuse cycles. Main mechanism: ligand exchange – sorption slightly enhanced due to co-ion and Donnan invasion mechanisms (Cl^- and SO_4^{2-}).	(Awual et al., 2014)
Nano-sized iron oxide coated sand	69.1% P removal without magnetic field application, 75% with.	20mL/min flow rate through column of 20cm height, 5cm width. Main mechanism: precipitation of Fe-P deposits on the surface of sand.	(Khiadani Hajian et al., 2013)
Chemically surface-modified silica filter	Effective up to 1.5L of influent with 36 filters (900g) to remove to P to below 1 mg/L. 20 seconds per 500mL with 36 filters.	Glass modified silica granules packed into 25g porous cylindrical filters. After regeneration, filters (36) unable to reduce P concentration to below 2 mg/L. Main mechanism: ion-exchange.	(Kim et al., 2012)

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Using sorbent materials for the removal and recovery of P for subsequent direct use as a fertiliser or soil amendment is attractive, provided that the sorbent material is economic and has adequate P affinity without retention of contaminants. If modifications are required to provide these, the cost and complexity of additional processing have to be considered. Rather few materials shown to be effective as sorbents for P are also suitable for direct application to agricultural land. Waste materials are an attractive option for having a low (or no) price and for their often wide availability, but incur the cost of compliance with regulation (European Union, 2003). Variability in composition is a further challenge. Also, materials showing high affinity for P in sorption studies may also have minimal potential for P release. Effective sorption is often brought about by high Fe or Al contents which, as discussed, may then limit solubilisation of P within the soil, or may be toxic in surrounding aquatic environments.

Other issues regarding the sorption of P from wastewaters is the co-sorption of toxic compounds that contain heavy metals/metalloids, or metals that compete with phosphate and other anions for sorption sites; selective recovery of P should therefore be a key goal of any recovery process. A Zn-Al LDH material reported in the literature provides an example for such selectivity. Intercalated with pyromellitic acid this sorbent achieved 97.4% selectivity toward P at pH 7 from complex solutions containing $H_2PO_4^-$, SO_4^{2-}, CO_3^{2-}, NO_3^- and Cl^- (Yu et al., 2015). Although this material showed a selective and effective P sorption compared to other options, the practicality of the material in terms of recyclability, usability or cost was not discussed. For innovation in sorbent technologies to translate to WWTP use, their potential feasibility should be assessed and demonstrated at an early stage. Their efficiency at low or high P concentrations should be assessed in relation to their suggested use; as filtration media in a tertiary process in the primary stream or for sorption of P within a side stream process treating sludge liquors and dewatered sludge, respectively. But their end use is an equally important consideration in developing sorbents for P recovery – the effective

bioavailability of P and its re-release into soil when used as a fertiliser or P-bearing soil amendment, or its potential for regeneration, i.e. re-use after desorption of P and its separate recovery. Sorption of P remains a flexible, efficient and potentially effective option; either as a potentially lower-cost alternative to crystallisation technologies, or as an additional technology that provides for enhanced P removal and recovery potential.

6 Bioavailability of recovered P products

Not all P in soil is bioavailable to plants and P is a key limiting nutrient in terrestrial ecosystems (Elser, 2012; Maltais-Landry et al., 2014). Phosphorus therefore plays a critical role in productive agriculture (Withers et al., 2014), but its plant availability however can often be low: it forms sparingly soluble fractions due to adsorption, precipitation or conversion to organic fractions in soil (Werner and Prietzel, 2015), via geochemical processes that depend on several soil properties such as the abundance of Ca, Al and Fe oxides, pH and organic matter content. The bioavailability of P in recycled P products can be assessed using chemical analogues for plant acquisition (i.e. using extractants) or more directly in pot or field trials. For P to be utilised by plants it must be soluble or solubilised, but solubility and potential bioavailability depends on a number of soil-related factors, so its assessment as an effective and suitable fertiliser should be undertaken in diverse environments. The use of Ca and Mg in crystallisation processes has been shown to have high potential for P recovery, owing to the solubility of precipitated Ca and Mg products in soil. The bioavailability of struvite has been more widely investigated: i.e. through cultivation of Chinese cabbage (Ryu et al., 2012); maize (Liu et al., 2011); maize and tomato plants (Uysal et al., 2014); corn and tomato plants (Uysal and Kuru, 2013). Struvite-P has been found to be relatively soluble and bioavailable across a wide range of pH conditions and soil types. Recovered Ca-P products have been investigated to a lesser extent.

Struvite can be considered as the better product compared with Ca-P, in terms of bioavailability. Through isotopic labelling techniques with ^{33}P, a reference hydroxyapatite and a recovered product partly composed of hydroxyapatite, were found to be less effective, in terms of the plant availability of P, than triple super phosphate (TSP), reference struvite and a recovered product composed of both struvite and hydroxyapatite (Achat et al., 2014a). However, using the same recovered products in pot and soil incubation experiments with slightly acidic soil growing ryegrass and fescue, both were as effective as TSP and the struvite reference material (Achat et al., 2014b). When the plant uptake of P derived from the applied products was compared with that derived from the TSP, the reference hydroxyapatite was found to have only 22% relative effectiveness, compared with 85-96% for the recycled products and 111% for the reference struvite. This was likely due to higher solubility of poorly crystallised phases of Ca-P associated with the recycled products (Achat et al., 2014b). The recovered P products containing struvite and Ca-P were derived from pig manures and dairy effluents.

The bioavailability of various recycled P products has also been compared with TSP and P-rock in pot experiments with maize in two contrasting soil environments (pH ($CaCl_2$) 4.7 and 6.6) over a period of 2 years. Recycled struvite products were found to be as effective as TSP in both soils, but the Ca-P product was only effective in the acidic soil (Cabeza et al., 2011). The restricted effectiveness of Ca-P to acidic soils is due to the enhanced disintegration of the P-rich material in higher H^+ concentrations and its relative stability in alkaline conditions. Similarly, an alkali sinter phosphate made from meat and bone meal was as effective as TSP in the acidic soil, while a cupola furnace slag was in the neutral soil (Cabeza et al., 2011). Both the SSA and a meat and bone meal ash had low effectiveness, in terms of P uptake and P concentration in the soil solution, and were comparable to rock-P. It was concluded that P products obtained through chemical processes were suitable for direct application as

fertilisers, especially struvite, and the ash products could be potential raw materials for P fertiliser production (Cabeza et al., 2011).

The thermochemical treatment of SSA is a promising technology in deriving heavy metal depleted residues containing P in bioavailable forms. Two SSA products thermochemically treated with either $MgCl_2$ or $CaCl_2$ were investigated for their plant availability in pot trials with ryegrass using ^{33}P (Nanzer et al., 2014). The shoot uptake of P from the Mg treated SSA was found to be higher than the Ca treated SSA (15.7 and 8.3 mg P/kg acidic soil, respectively). The effectiveness of the Mg treated SSA relative to a water-soluble P fertiliser was 88% in an acidic soil, 71.2% in a neutral soil but was reduced to 4% in an alkaline soil (Nanzer et al., 2014).

Large gaps still remain in the understanding of the release and plant availability of P in soils from recovered products derived from WWTPs. From review, the use of indirect isotopic labelling techniques would appear to be the best method in assessing the contribution of recovered-P to plant available P in soil and P utilised by the plant. Further investigation and empirical information regarding the availability, plant uptake and cycling of P in soils related to the application of recovered products and residues will lead to a greater understanding and confidence in their use as alternatives to inorganic-P derived fertilisers. It is additionally important that both the removal process and reuse of P are considered on a case-by-case basis – not all recovery processes will be applicable to all wastewaters, and similarly not all recovered products will be equally effective across different soil environments. As sorbent materials can be derived from a wide variety of materials and processes, providing a myriad of physical and chemical characteristics, P sorbed to and within the surface and structure of these solids may have wide ranging applications.

7 Conclusions

The diminishing quantity and quality of P-rock reserves, and the eutrophication of water bodies, are instigating a critical need to recover P from WWTPs in forms suitable for agricultural application. There are numerous recovery options that vary in application (i.e. sludge, sludge liquor, primary stream, SSA) and technology used (precipitation, EBPR, AD, wet chemical extraction, thermochemical treatment). The chemical precipitation of struvite and Ca-P, from the digested EBPR sludge stream, are the favoured routes that are technologically well developed and already in operation in a number of WWTPs. The mono-incineration of sludge followed by thermochemical treatment of the SSAs are also promising steps in the production of secondary P residues suitable as a detoxified P fertiliser.

EBPR currently forms the basis of chemical crystallisation technologies in providing a process stream of suitable concentration for efficient P recovery. The minimisation of Fe and Al, especially where P is to be recovered from anaerobic digestate, is important to maximise P release. Where chemical accumulation processes are required to be operated due to spatial, economic or infrastructural requirements the metal salt applied and the resulting sludge composition should be considered regarding the suitability of the sludge residue for processing by the fertiliser industry or its use directly as a detoxified residue after thermochemical treatment.

Technologies such as thermochemical treatment, wet chemical extraction and electrodialysis may be used to increase the total recovery potential to around 90%, and in some cases, have been shown to be economically feasible. However, the present cost of some existing and novel technologies is not yet offset by a marketable product due the current omission of recovered products from fertiliser legislation. Where P must be removed on in some cases recovered, to comply with statutory limits and regulation, a range of approaches will be

valuable and necessary despite not being profitable – the inclusion of recovered P products such as struvite and ashes in to the revised fertiliser legislation will then create a value and a market for these products. This is important in enabling recovered-P products to substitute and compete with primary fertilisers on the market and could foreseeably require subsidisation or regulatory forcing until an increase in price of primary fertilisers ensures that widespread agricultural adoption is economical.

Around 90% of the incoming P load can be incorporated into sewage sludge, however to consistently achieve P limits of <1 mg/L, WWTPs require a further removal of P before discharge, with future legislation foreseeably requiring increasingly lower concentrations of P in discharge. Consequently, a gap in wastewater treatment strategy has presented itself; the "polishing" of effluents, other than by additional chemical dosing, in a tertiary treatment setting where EBPR may not be able to reliably meet required concentrations. Experimental technologies (ion-exchange, novel sorption processes, membrane filtration, etc.), although not yet commercially operational, may become key in providing an enhanced P removal and recovery potential. Sorbents, if effective, may easily be incorporated into existing infrastructures and may provide alternatives to technologies unachievable at smaller WWTPs – currently the precipitation of struvite/ Ca-P can only be practically applied at large WWTPs operating EBPR. The focus of experimental technologies and especially sorption processes is deriving recovered-P products or residues of suitable purity, form, economy and bioavailability for their safe and effective application as fertiliser to agricultural land.

Struvite compares well to TSP and other mineral-P fertilisers in pot trials under a range of soil pH values, but full field trials and longer term tests are still lacking. The application of recovered-P products and residues to soils and their use by crops needs further investigation and empirical information – understanding the bioavailability and availability of recovered P and its use by plants in a wide range of soils and environments is important to increase

confidence in the precise and effective use of these products as a substitute for conventional inorganic-P derived fertilisers. This will be vital for the widespread recovery of P and the adoption of recovered-P as fertiliser.

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Graphical Abstract